

AGRICULTURAL RESEARCH INSTITUTE

PUSA







# THE JOURNAL

OF THE

# American Chemical Society

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VOL. XLIII

JULY—DECEMBER  
1921

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# THE JOURNAL

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### THE ACTION OF ULTRA-VIOLET LIGHT ON COLLOIDAL PLATINUM.

By ELLWOOD B. SPEAR, P. F. JONES, A. S. NEAVE AND M. SHLAGER.

Received December 31, 1919.

Considerable experimental work has been recorded in the literature on the curious and as yet unexplained coagulating action of ultra-violet,  $\beta$ , and X-rays on substances in the colloidal state.<sup>1</sup> Extraordinary as this effect appears, the case is still more complicated by the fact that these same rays have been employed by many investigators to produce certain hydrosols from the corresponding metals.<sup>2</sup> Moreover in some respects the evidence of one author often contradicts the results obtained by others, so that the entire subject is in a decidedly unsatisfactory state.

<sup>1</sup> Carey-Lea, "Kolloidales Silber und die Photohaloide." Doelter, "Das Radium und die Farben," Henri und Mayer, *Compt. rend.*, **138**, 521 (1903); Jorissen and Woudstra, *Z. Chem. Ind. Kolloide*, **8**, 8-11 (1911); Farmer and Parker, *This Journal*, **35**, 1524 (1913); Long, *Kolloid-Z.*, **14**, 130-8 (1914); Stintzing, *Kolloidchem. Beihefte*, **6**, 231 (1914); Schumm, *Kolloid-Z.*, **15**, 103 (1914); Nordenson, *Z. physik. Chem.*, **90**, 803-37 (1915); Pihlbad, *ibid.*, **92**, 471-95 (1917).

<sup>2</sup> Leonard and Wolf, *Ann. Phys.*, [3] **37**, 443 (1880); Svedberg, *Ber.*, **42**, 4375 (1909); Jaccquard, *Proc. Acad. Sci. Amsterdam*, **21**, 131-7 (1918).

It seemed desirable, therefore, to make a study of this interesting field and to correlate and harmonize, if possible, the conflicting evidence.

With this end in view it was decided to begin the investigation with

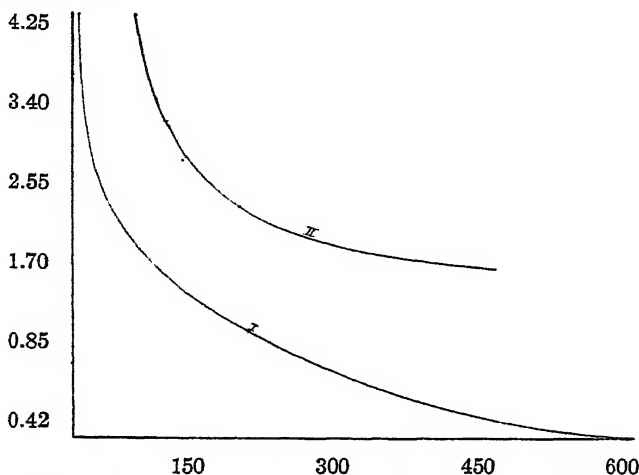


Fig. 1.—The ordinates represent the concentration of NaCl in millimols per liter in the reaction mixture. The abscissas represent the time in minutes necessary for the coagulation of one-half of the platinum in Solution B. Temperature of experiments = 20 to 22°. Curve I shows the results with the rays, Curve II without the rays.

as simple a case as possible, namely, the effect of ultra-violet rays on colloidal platinum, because the metals of the platinum group may be readily obtained in the colloidal state with a degree of purity greater than that of any other class of substances.

### Experimental Method.

In order to determine the effect of the rays a carefully prepared reaction mixture was divided into two parts. One of these was placed in a crystallizing dish upon the submerged stage of a cooling system described later, covered with a quartz plate, the stirring device started and the ultra-violet light turned on. The other half of the sample, contained in a second crystallizing dish, was either placed in a thermostat, or it was set beside the first one on the submerged stage and covered with a glass plate to cut off the ultra-violet rays. Thus the two samples were treated exactly alike except that one was subjected to the action of light plus ultra-violet rays, while the other was exposed only to the light that would penetrate glass.

All reaction mixtures were invariably made up to a definite volume, usually 25 cc., at the beginning of each experiment.

by diluting 20 cc. of the stock solution with conductivity water, or with a solution of electrolyte in case the latter was employed.<sup>3</sup>

**The Conductivity Water.**—The water employed in this work was redistilled from 0.02 *N* alkaline permanganate solution through block tin condensers. One sample of water, after standing for 3 months in a well-stoppered, hard-glass bottle, had a conductivity of  $4.10^{-6}$  mhos while another, immediately after it had been collected, had a conductivity of  $5.10^{-7}$  mhos.

**Platinum Solutions.**—Platinum hydrazols were prepared by the well-known electrical colloidation method according to Bredig.<sup>4</sup> The solutions were colored a rich brown and one of them at least was so stable that all the platinum had not settled out in two years' time. The concentration of the platinum in solution, determined by a method previously described by one of us,<sup>5</sup> is given in connection with the various curves.

The conductivity of the platinum solutions was, of course, greater than that of the water from which they were made. Platinum solution B, after standing for 3 months in a well-stoppered, hard-glass bottle, had a conductivity of  $1.2 \times 10^{-5}$  mhos. Platinum solution C, after standing for 2 months, had a conductivity of  $2.2 \times 10^{-5}$ .

**The Electrolytes.**—Colloidal platinum solutions are so sensitive to bivalent and trivalent ions, such as  $\text{Ba}^{++}$  and  $\text{Al}^{+++}$  that it was found more convenient to employ sodium chloride as the electrolyte during accurate measurements. Nevertheless, some runs were made with barium chloride solutions and results of the same general nature were obtained. The sodium chloride solutions were made from conductivity water and sodium chloride that had been specially prepared for analytical standardizations.

**Ultra-violet Light and Cooling System.**—The source of the ultra-violet light was a Cooper-Hewett 220-volt quartz lamp. This was enclosed in a wooden case which had the dimensions  $60 \times 90 \times 120$  cm. The front of the case was provided with swinging doors, and each door was fitted with a red glass window. By this means the operations could be watched without endangering the eyes, as red glass is particularly efficacious for cutting off the ultra-violet rays.

The lamp emits very considerable heat, so that a cooling system was necessary in order to maintain a constant temperature. This was secured by partially submerging the crystallizing dish containing the reaction mixture in a pneumatic trough placed inside the box. The trough was filled with water running at constant level.

<sup>3</sup> In some of our first experiments no quartz plate was used, so that the light was allowed to strike directly upon the surface of the liquid. During protracted runs of this nature, after 16 hours, small amounts of conductivity water were added from time to time in order to make up for the slight loss of water due to evaporation.

<sup>4</sup> Bredig, *Chem.*, 1898, p. 195.

NAL, 30, 195 (1908).

Another important factor to be considered is the distance of the surface of the reaction mixture from the source of light. This distance was maintained throughout our experiments at 15 cm. in order that the different runs might be comparable. Moreover, ultra-violet rays are absorbed almost entirely in the surface layers of the platinum solutions, so that it was necessary to stir the liquid in order to subject all portions to the action of the rays. This was effected by means of a small piece of platinum foil rotated by an electric motor.

**The End-point.**—If sufficient sodium chloride, which we will call the critical value, is added to cause the coagulation of platinum solutions within a few minutes, a change of color from brown to turbid gray takes place instantly on mixing the two solutions. The same change of color may be brought about by any amount of sodium chloride below this critical value, but a much longer time is necessary for the more dilute solutions of the salt. When these gray solutions are allowed to run through filter paper the filtrate is clear and colorless. During most of our work the experiment was allowed to proceed until such a clear colorless filtrate was obtained.

When very pure platinum solutions without added electrolyte were treated by the rays the time required for complete coagulation was sometimes as long as 20 to 30 hours. In such cases it was found more convenient to choose as the end-point the time necessary to reduce the color to that of a standard solution containing one-half the concentration of platinum possessed by the original reaction mixture. The standard solution was made by diluting a portion of the stock solution until the concentration of platinum was one-half that of the reaction mixture. The comparison of colors was made, of course, according to the usual colorimetric methods.

**Cleansing the Apparatus.**—All vessels that came in contact with the conductivity water or the platinum solutions were carefully cleaned with chromic acid, thoroughly rinsed with conductivity water and finally treated mouth downward for 30 minutes with steam from conductivity water.

### Discussion of Results.

For the sake of economizing space, only a few of our results are given in Tables I and II. The data for a single series of experiments, Solution B, Table I, have also been reproduced in the form of curves in Fig. 1. Information concerning the concentrations of colloidal and electrolytic solutions, also the temperature and the time of coagulation are given in connection with the tables and the curves. The time reported is the average of 2 to 5 separate determinations.



TABLE I.

Temperature of runs = 20 to 22°.

Millimols. NaCl per liter in mixture.	Solution A. Conc. Pt.=0.024 g. per liter in mixtures.			Solution B. Conc. Pt.=0.038 g. per liter in mixture.			Solution C. Conc. Pt.=0.046 g. per liter in mixture.		
	<i>t</i> = Time in minutes for the coagulation of one-half the platinum.								
	<i>t</i> <sub>1</sub> .			<i>t</i> <sub>3</sub> .			<i>t</i> <sub>5</sub> .		
	With rays.	Without.	Ratio.	With rays.	Without.	Ratio.	With rays.	Without.	Ratio.
			$\frac{t_2}{t_1}$ .			$\frac{t_4}{t_3}$ .			$\frac{t_6}{t_5}$ .
4.25	15	135	..	7	64	...	...	...	...
3.40	24	269	11	15	90	6.0	45	75	1.6
2.55	48	480	..	30	145	...	...	...	...
1.70	59	804	13	90	450	5 0	60	171	2.8
0.85	90	1270	..	240	...	...	105	240	...
0.42	120	..	..	349	...	...	201	...	...
0.21	157	..	..	...	...	...	...	...	...
0.00	...	..	..	600	<i>a</i>	...	...	...	...

<sup>a</sup> The platinum was not completely coagulated in 2 years' time when Solution B was kept in the laboratory desk. Solutions A and C were kept for several months without any very appreciable coagulation of the platinum.

TABLE II.

Solution D.

Temperature = 16.8 to 17°.

With electrolyte present the acceleration due to the ultra-violet light is greater in dilute than in more concentrated colloidal solutions. Solution D showed very slight coagulation of the platinum in 2 months when no electrolyte was added and the rays were not employed.

Conc. NaCl in Millimols per liter.	Conc. Pt. in grams. per liter.	<i>t</i> = Time in minutes for complete coagulation of Pt.		Ratio
		With rays. <i>t</i> <sub>1</sub> .	Without. <i>t</i> <sub>2</sub> .	
17.1	0.081	18	35	1.9
17.1	0.073	35	93	2.6
17.1	0.064	64	180	2.8

In any consideration of the results of our experiments it should be constantly borne in mind that the effect of the rays as shown by our data is relative and not absolute. The magnitude of the influence depends upon several factors which we have endeavored to hold constant, namely, the intensity of the rays, the distance that separated the reaction mixture from the source of the ultra-violet light, the rate and manner of stirring and the temperature. However, in spite of these reservations with regard to magnitude, three general conclusions of a qualitative nature may be drawn from the experimental evidence. These three conclusions will be discussed in order.

I. Ultra-violet light greatly hastened the coagulation of colloidal platinum without the addition of any electrolyte, except possibly the carbon dioxide of the air, or that due to the dissolution of the hard glass from the

container. This conclusion is justified by the fact that in Solution B the platinum was one-half coagulated by the rays in 10 hours, while without the rays the platinum was not completely coagulated in 2 years. In the case of another solution, not previously referred to in this article, which had a slightly different concentration, even a shorter time was required to coagulate one-half the platinum.<sup>6</sup>

II. The second conclusion is that when electrolytes are present their influence on the coagulation is very greatly accelerated by the action of the ultra-violet light. This is clearly brought out by a comparison of Cols. 2, 5 and 8 of Table I, with Cols. 3, 6 and 9, respectively. The acceleration is even more apparent in Fig. 1, where Curve I represents the concentration of the electrolyte in millimols per liter plotted against the time in minutes required for the coagulation of one-half of the platinum in Solution B, and Curve II represents the same thing for Solution B where the ultra-violet light was not employed.

III. A third conclusion to be drawn from our results is covered by the statement that the accelerating action of the rays is greater in dilute solutions of the colloid than it is in the more concentrated. This is clearly indicated by the ratios in Cols. 4, 7 and 10, Table I, at two different concentrations of sodium chloride 3.40 and 1.70 millimols per liter, and further substantiated in Table II for three different concentrations of the same colloidal solution where the electrolyte was kept constant.<sup>7</sup>

This result might be anticipated in part when it is remembered that the ultra-violet light can penetrate into the dilute solutions of the colloid farther than it can into the more concentrated. It is unsafe to conclude, however, that this is the sole reason for the observed facts. As suggested by Nordenson<sup>1</sup> it may very well be that the rays react upon the medium rather than on the platinum particles, in which case the accelerating action should be greater when there are fewer colloidal aggregates to absorb the ultra-violet light.<sup>8</sup>

<sup>6</sup> In order to determine whether or not the rays could coagulate colloidal platinum without the aid of some electrolyte other than water itself, it would be necessary to exclude the air during the distillation of the water, the formation of the colloidal platinum, and finally the treatment with the rays. The experiment would be difficult but not impossible.

<sup>7</sup> It is unfortunate that our work was permanently interrupted before the concentrations could be varied over a greater range.

<sup>8</sup> During the progress of work as yet unpublished it was found that the conductivity of sodium chloride solutions was slightly increased by the action of ultra-violet light. Minute quantities of hydrogen peroxide were also found to be present. Because these effects were so inappreciable it does not seem possible that the extraordinary acceleration of the rays can be attributed to these causes.

## Summary.

In this article we have presented experimental evidence to show that ultra-violet light will precipitate colloidal platinum out of solutions that are free from electrolyte except the carbon dioxide of the air, or that due to the dissolution of hard glass.

We have also shown that when electrolytes are present their precipitating effect is very greatly accelerated by the action of ultra-violet rays.

The action of the ultra-violet light was shown to be greater in dilute solutions of the colloid than in the more concentrated.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 360.]

## THE APPLICATION OF IDEAL SOLUTION EQUATIONS TO DILUTE AQUEOUS SOLUTIONS.

BY JAMES KENDALL.

Received April 27, 1920.

The relative lowering of the vapor pressure of water by addition of a normal, non-volatile solute is such a fundamental point in the study of solutions that one would expect physical chemists, at this late date, to have agreed upon some definite theoretical treatment of the topic. An examination of the literature will show, however, that this is far from being the case. In the following pages a brief analysis of the present situation is made, and an explanation of existent discrepancies indicated. The erroneous interpretation now given to certain equations derived from the law governing vapor-pressure depression for ideal solutions, when applied to aqueous solutions, is also discussed.

**The Dilute-Solution Equation.**—Most introductory text-books<sup>1</sup> follow Arrhenius<sup>2</sup> in deriving the equation for the vapor pressure of highly dilute solutions from van't Hoff's gas law for osmotic pressure, obtaining the relation<sup>3</sup>

$$(p_0 - p) / p_0 = n / N \quad (1)$$

where  $p_0$  is the vapor pressure of pure solvent,  $p$  the vapor pressure of solution, and  $n/N$  is the ratio of the number of solute molecules to the number of molecules which the solvent would produce *if converted into*

<sup>1</sup> For example, Walker, "Introduction to Physical Chemistry," 1913, p. 193; Lehfeldt, "Physical Chemistry," p. 29.

<sup>2</sup> Arrhenius, *Z. physik. Chem.*, 3, 115 (1889).

<sup>3</sup> This relation is strictly valid only for solutions of infinite dilution, constituting the limiting case of the more exact equation:  $\ln (p_0/p) = n/N$ . The difference between the calculated values for the two forms of the equation is, however, inappreciable even for a fairly concentrated solution. For an example see Lehfeldt, *op. cit.*, p. 31.

*vapor*. The words in italics are vitally significant in the case of an associated solvent such as water.<sup>4</sup>

The experimental data for dilute aqueous solutions (although few determinations of a high order of accuracy are available) are in good agreement with the above equation. The results of Frazer and Lovelace<sup>5</sup> for mannite solutions may be cited:<sup>6</sup>

$T$ , °C.	Conc. (wt. molar).	$p_o - p$ , mm.	$p_o$ , mm.	$(p_o - p)/p$ , (obs.).	$(p_o - p)/p_o$ , (calc.).
20.008	0.4	0.122	17.548	0.070	0.072
20.036	0.5	0.156	17.578	0.089	0.089

**The Ideal-Solution Equation.**—The tendency in recent advanced textbooks<sup>7</sup> is to present the subject from a different standpoint, namely the ideal-solution equation.<sup>8</sup> This postulates that, above an ideal solution, the vapor pressure of each molecular species is proportional to its molar fraction in the solution, or,

$$(p_o - p) / p_o = n / (N + n), \quad (2)$$

where  $n$  and  $N$  represent the numbers of molecules of non-volatile solute and volatile solvent, respectively, *existent in the solution*. Although water is not an ideal but an associated solvent, it has been generally accepted that aqueous solutions may be treated as ideal, within the limits of experimental error, provided that the solute concentration is not too high.<sup>9</sup> Not only has the above ideal equation been extended to aqueous solutions, consequently, but formulas for the representation of osmotic pressure, freezing-point lowering and boiling-point elevation measurements have also been derived therefrom, which have been found to furnish very satisfactory agreement with the experimental data even for fairly concentrated solutions of normal solutes, where the deviations from the "dilute-solution equations" of van't Hoff are quite considerable.<sup>10</sup>

It is important to note the significance which has been attached by workers in these fields to the quantity  $N$  in the ideal equation (2) when applied to aqueous solutions.  $N$  has been almost universally regarded as still

<sup>4</sup> "It must be emphasized that the number of molecules  $N$  in the above equation does not denote the number of liquid molecules in the solvent, but only the number of gaseous molecules derivable from the liquid. This caution is necessary, because it has frequently been supposed that the equation enables us to determine the molecular weight of the liquid solvent, which is not the case." Walker, *op. cit.*, p. 194.

<sup>5</sup> Frazer and Lovelace, *THIS JOURNAL*, 36, 2439 (1914).

<sup>6</sup> For further examples see Jellinek, "Lehrbuch d. phys. Chem.," 2, p. 779 (1915).

<sup>7</sup> E. g., Washburn, "Principles of Physical Chemistry," 1915, p. 146.

<sup>8</sup> Van Laar, *Z. physik. Chem.*, 15, 457 (1894); Gibbs, *Nature*, 60, 461 (1897); G. N. Lewis, *Proc. Am. Acad.*, 43, 259 (1907).

<sup>9</sup> The approximate limits for solutes of various types have been indicated by Washburn, *op. cit.*, p. 141.

<sup>10</sup> See Findlay, "Osmotic Pressure," 1919, p. 65; Frazer and Myrick, *THIS JOURNAL*, 38, 1907 (1916).

representing the number of molecules of solvent actually existent in the solution.<sup>11</sup> Under this interpretation, since water is admittedly highly associated in the liquid state at ordinary temperatures, while water vapor is to all intents and purposes entirely monomolecular,<sup>12</sup> the value for  $N$  for any given solution must be quite different according to Equation 2 from what it is in Equation 1.

Now it is true that the essential incompatibility of dilute and ideal solution equations for solutions of finite concentration has long been recognized,<sup>13</sup> but it is also axiomatic that as the solute concentration approaches zero the divergences between them must be vanishingly small.<sup>14</sup> For an associated solvent such as water, however, the divergences between Equations 1 and 2, if  $N$  has *not* the same significance in each, are fundamental and persist right up to the very highest dilutions of solute. In other words, the ideal-solution equation, as it is at present being interpreted, is in utter disagreement with the dilute-solution equation for all aqueous solutions and hence cannot be in accordance with the existent experimental data. This is a point which has escaped attention hitherto,<sup>15</sup> but clearly one which requires immediate rectification.

**Reconciliation of the Ideal-Solution Equation with the Dilute-Solution Equation and with the Experimental Data.**—The necessary reconciliation can be effected by modifying the present erroneous interpretation given to Equation 2 when applied to aqueous solutions. Although liquid water is a mixture of associated molecules of the general type  $(\text{H}_2\text{O})_q$  and simple monomolecular  $\text{H}_2\text{O}$ , yet the latter molecular species is the only variety which is appreciably volatile

<sup>11</sup> An exception is found in the work of Washburn and Heuse, *THIS JOURNAL*, 37, 319 (1917). These investigators noted that it was necessary to employ a value "not appreciably different" from 18 for the molecular weight of water in deriving an equation for calculating osmotic pressures from vapor-pressure depression data.

<sup>12</sup> Kendall, *THIS JOURNAL*, 42, 2477 (1920); Menzies, *ibid.*, 43, 851 (1921).

<sup>13</sup> See, particularly, G. N. Lewis, *ibid.*, 30, 668 (1908). The ideal-solution equation is called by Lewis the "modified equation of Raoult," but since the name of Raoult has also been associated with the dilute-solution equation it has been thought advisable to avoid confusion here by giving the formulas under discussion impersonal titles. Raoult first expressed his experimental results by an equation similar in form to Equation 1 above, the subsequent modification to Equation 2 being made *empirically* to allow the equation to be extended to very concentrated solutions (see Ostwald, *Solutions*, 1891, p. 168-73).

<sup>14</sup> Thus Equations 1 and 2 for non-associated liquids obviously become identical when  $n$  is negligible in comparison with  $N$ .

<sup>15</sup> Presumably because the interest of investigators has been focused almost exclusively upon derived equations (osmotic pressure and freezing-point depression relationships) in which a factor which compensates for association is assumedly present, as will be discussed in a later section.

at ordinary temperatures.<sup>16</sup> Hence the vapor pressure  $p$  of any aqueous solution must be directly proportional, not to the total mol fraction of solvent present, but to the mol fraction of monomolecular  $\text{H}_2\text{O}$  existent in the solution. At ordinary temperatures this quantity is undoubtedly extremely minute,<sup>17</sup> owing to the high degree of association of water in the liquid state. On addition of solute it will be still further reduced, and at first sight this reduction would appear to follow quantitatively the current interpretation of Equation 2.<sup>18</sup> We must take into consideration the fact, however, that addition of solute also involves a shift in the equilibrium  $(\text{H}_2\text{O})_q \rightleftharpoons q(\text{H}_2\text{O})$ , a partial disassociation of complex to simple molecules taking place. The effect of this shift in the association equilibrium upon the vapor-pressure depression equation is examined below.

In pure water, let the mol fraction of non-associated  $\text{H}_2\text{O}$  equal  $N$ , and associated  $(\text{H}_2\text{O})_q$  equal  $1-N$ . In a solution, let the mol fraction of solute be  $n$ ; of  $\text{H}_2\text{O}$ ,  $N-x$ ; of  $(\text{H}_2\text{O})_q$ ,  $1-N-n+x$ .

For both solvent and solution we have, applying the mass-action law to the association equilibrium:  $(\text{conc. } \text{H}_2\text{O})^q / (\text{conc. } (\text{H}_2\text{O})_q) = K$ . Hence:  $N^q / (1-N) = (N-x)^q / (1-N-n+x)$ .

If sufficiently dilute solutions are considered, powers of  $x$  higher than the first can be neglected, and we obtain

$$x = nN / (N + q(1-N)).$$

But if the vapor pressure is due only to non-associated  $\text{H}_2\text{O}$ , its lowering will be proportional to the lowering of the mol fraction of non-associated  $\text{H}_2\text{O}$  in the solution; i. e.,  $(p_0 - p) / p_0 = x / N = n / (N + q(1-N))$ .

Since  $q$  is not known, it is impossible to evaluate this equation directly for any solution, but we can test its applicability by comparing it with the dilute solution equation. For, according to this equation, if  $a$ ,  $l$  and  $c$  be the numbers of molecules of solute,  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_q$  respectively in a given weight of solution  $(p_0 - p) / p_0 = a / (b + qc)$ . And since at high dilutions the shift in the water equilibrium will not significantly

<sup>16</sup> This is indicated by the normal behavior of water vapor (Kendall, *loc. cit.*). It is of interest to note that all of our currently accepted equations for aqueous solutions are derived with the use of the assumption that water vapor obeys the gas laws exactly, which cannot be valid unless water vapor is essentially monomolecular.

<sup>17</sup> Shown by the low vapor pressure of water at ordinary temperatures. From a comparison of the properties of corresponding organic derivatives, we may conclude that monomolecular  $\text{H}_2\text{O}$  should be more volatile than  $\text{H}_2\text{S}$ . Walden (*Z. physik. Chem.*, **55**, 683 (1909)) has calculated the boiling point for simple  $\text{H}_2\text{O}$  as  $-120^\circ$ . Van't Hoff ("Lectures on Theoretical and Physical Chemistry," Part III, p. 50) obtained a still lower value,  $-207^\circ$ .

<sup>18</sup> The ratio of the mol fraction of simple  $\text{H}_2\text{O}$  to the total mol fraction of solvent being regarded as a constant.

affect the *total* number of water molecules present, we have (within error limits),  $a/(b + qc) = n/(N + q(1 - N))$ .

Hence the ideal-solution equation is brought into agreement with the dilute-solution equation and consequently also with the experimental data for dilute aqueous solutions.

In applying ideal solution equations to dilute aqueous solutions we must, therefore, proceed just as if water were a non-associated liquid, the shift in the equilibrium  $(\text{H}_2\text{O})_q \rightleftharpoons q(\text{H}_2\text{O})$  compensating for the effect of association upon the molar fraction. In other words, it must be recognized that the ratio  $p/p_0$  is essentially independent of the association factor of the solvent. The effect of this on certain derived relationships may now be briefly considered.

**The Ideal Osmotic Pressure Equation.**—The failure of the dilute solution equation  $\Pi V = RT$  to represent the osmotic pressures of solutions of finite concentration is now generally conceded. In its place we have a more exact equation of the form:<sup>19</sup>

$$\Pi V_0 = -RT \ln(p/p_0) \quad (3)$$

where  $V_0$  is the molar volume of the solvent, a small correction factor for compressibility being omitted. To this equation the ideal solution principle that the ratio  $p/p_0$  represents the mol fraction  $x$  of volatile solvent has been applied, with the result:

$$\Pi V_0 = -RT \ln nx \quad (4)$$

In the application of this formula to dilute aqueous solutions, considerable energy has been expended in laborious calculations as to the effect of association.<sup>20</sup> The comforting conclusion has been reached that it makes little difference what value for the association factor for water is taken, since any variation in  $x$  (the mol fraction of solvent) on the right-hand side of the equation is counterbalanced by a corresponding variation in  $V_0$  (the molar volume of the solvent) on the left-hand side.<sup>21</sup>

In view of the result derived above, that  $p/p_0$  is independent of the association factor and that  $x$  is consequently a *fixed value*<sup>22</sup> for any given solution, this conclusion would appear to become invalid. Most fortunately (as it happens) a second error has been made which evens up matters. An examination of the thermodynamic cycle upon which Equations 3 and 4 are based<sup>23</sup> discloses the fact that  $V_0$  refers to the volume occupied by one

<sup>19</sup> Findlay, *op. cit.*, p. 55.

<sup>20</sup> For example, see Frazer and Myrick, *THIS JOURNAL*, 38, 1907 (1916).

<sup>21</sup> *E. g.*, with a weight-normal solution of cane sugar at 20° the values  $\Pi = 23.50$  for monomolecular water and  $\Pi = 23.64$  for water with an association factor 1.65 are obtained. The experimental value is  $\Pi = 26.64$  (Findlay, *op. cit.*, p. 64-5).

<sup>22</sup> The value obtained by "assuming" all water to be existent as monomolecular  $\text{H}_2\text{O}$ .

<sup>23</sup> See Washburn, *op. cit.*, 1915, p. 409-10.

gram-molecular-weight of *water vapor* after condensation, and is therefore also independent of the association factor for *liquid water*.

It seems almost impossible that such a fundamental point should not have been noticed before, but reference to recent literature will show that the "association factor" is still regarded as a stumbling block in the study of abnormalities in the osmotic pressure in aqueous solutions. Its removal from the sphere of action will, it is hoped, facilitate the long-delayed attack upon the main abnormality—hydration. The early workers<sup>24</sup> in this field have certainly met with more than their fair share of good fortune in the fact that their assumptions, although founded upon a wrong basis, are practically valid as a consequence of the mutual cancellation of the two errors involved.

**The Ideal Freezing-point Depression Equation.**—In the application of the ideal solution formula—

$$\ln x = (Q/R) \cdot (1/T - 1/T_0) \quad (5)$$

for freezing-point depressions, similar mistakes have been made.  $Q$  (the molar heat of fusion) has been regarded as a factor varying with association, although as derived in the thermodynamic cycle it refers to one gram-molecular-weight of *condensed water vapor*. In the same way  $x$  is considered as a variable,<sup>25</sup> compensating for variations in  $Q$ . In actual fact, both  $x$  and  $Q$  are *independent* of association in the liquid state, and all values derived with the use of arbitrary association factors (even though they differ but slightly from the correct values) are misleading.

### Summary.

The essential incompatibility of the fundamental ideal-solution equation, as applied at present to dilute aqueous solutions, with the dilute-solution vapor-pressure depression equation and with the results of experiment has been pointed out.

It has been shown that the discrepancy disappears when due notice is taken of the fact that the vapor pressure of water at ordinary temperatures must be ascribed practically entirely to its monomolecular fraction, the shift in the equilibrium  $(\text{H}_2\text{O})_g = q(\text{H}_2\text{O})$  on addition of solute counterbalancing the effect of the association upon the molar fraction.

Some fundamental errors in the present application of ideal osmotic-pressure and freezing-point depression equations to dilute aqueous solutions have also been corrected.

NEW YORK, N. Y.

<sup>24</sup> For example, Callendar, *Phil. Trans.*, 209A, 177, 319 (1908); *Trans. Faraday Soc.*, 8, 1 (1912).

<sup>25</sup> Roozeboom, "Heterogene Gleichgewichte," 1904, vol. 2, pp. 306-7. The present author pleads guilty to having himself erred on this point (see Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2310 (1917)), but good company is plentiful.



[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ARIZONA  
AND NEW HAMPSHIRE COLLEGE.]

## THE CONCENTRATION OF THE ERBIUM EARTHS.

BY PAUL H. M.-P. BRINTON AND C. JAMES.

Received September 16, 1920.

An investigation of four different methods for the concentration of the less basic rare earths resulted in the discovery of two of the most rapid procedures for this purpose. The methods examined were (a) formation of basic nitrates; (b) crystallization of chlorides from 1:1 hydrochloric acid; (c) formation of basic chlorides; and (d) formation of basic thio-sulfates. Of these methods (a) and (b) proved to be the best, and the exact manner in which they were carried out is described below.

(a) **Formation of Basic Nitrate.**—When following the old plan involving fusion of the nitrate for separating erbium from yttrium, it has been pointed out from time to time that the best results were obtained when the entire melt went into solution in boiling water, and deposited the basic nitrate in small crystals upon cooling or evaporation. The basic nitrates are more soluble in hot dilute solutions and less soluble in hot concentrated or cold dilute solutions. However, when the mixture consists mainly of the erbium earths, the basic nitrate, if there is much of it, will remain insoluble. The fact that the best results were obtained when the basic nitrate dissolved entirely in the excess of nitrate solution makes it obvious that the same results should be obtained by treating the solution with sodium hydroxide solution.

In order to test this a solution of yttrium nitrate, containing a little erbium, was heated to boiling, treated carefully with a fairly strong solution of sodium hydroxide and thoroughly boiled. The yttrium hydroxide which first precipitated soon dissolved. The addition of the sodium hydroxide solution was continued until minute crystals of the basic nitrate were observed swirling through the liquid. The whole was then set aside to cool. Upon examining the vessel next morning it was found to be lined with a mass of needle-like crystals of the basic nitrate radiating towards the center. These were filtered off, dissolved in the least amount of nitric acid, and the solution heated to boiling and treated with sodium hydroxide solution as described above. The basic nitrate crystals from this solution dissolved in nitric acid giving a rose-red solution showing intense absorption bands of erbium. This, together with a determination of the equivalent, showed that erbium was rapidly collecting in this portion.

The original filtrate was treated several times with sodium hydroxide solution. Although the concentration of the nitrates was kept high, the absorption bands soon began to fade.

Since this method worked so well for the yttrium-erbium mixture, it was next tried out with yttrium, holmium and erbium with good results.

During the fractionation, fractions of the same rare earth content were mixed together. Fractionations of this type are intermittent and do not run so smoothly as the simple crystallization methods. After further work it was noticed that two kinds of basic nitrates were obtained, one as described above, and another which separated from the boiling liquid during evaporation. The former compound readily dissolved in the diluted mother liquor at the boiling point, while the latter did not.

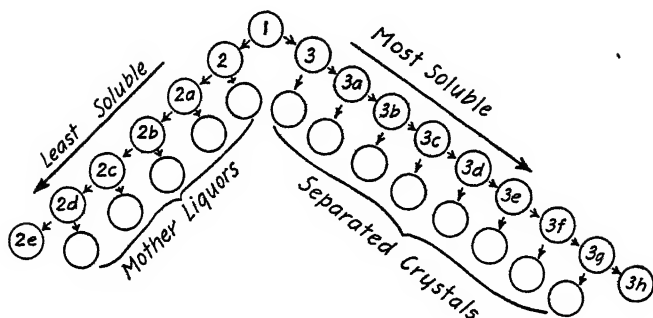
Some of the basic nitrate and a solution of the nitrates which appeared to be of the same rare earth content were next selected. The nitrate solution was diluted somewhat, heated to boiling, the basic nitrate gradually added and the clear solution evaporated to the original volume and allowed to cool. After standing for some time, a quantity of basic nitrate separated out which, when examined in the spectroscope, showed as great an increase in the erbium content as the former sodium hydroxide fractionation or the old classic fusion of the nitrate gave.

It must be admitted that this method when used with the fractional crystallization plan requires much more practice than the crystallization of double nitrates, bromates or ethyl-sulfates. However with a little experience the time saved is very great.

(b) **The Crystallization of the Chlorides.**—For the concentration of the more basic erbium earths, holmium and dysprosium from yttrium, the authors recommend the fractional crystallization of the chloride from constant-boiling hydrochloric acid. The speed of separation was first observed during the preparation of a chloride from an yttrium oxide containing some holmium and dysprosium. The solution of the chlorides was evaporated, cooled in snow and saturated with hydrogen chloride for 20 to 30 minutes. The crystals which formed were removed by suction, the filtrate was again saturated with hydrogen chloride, the crystals were removed, and the whole process was repeated several times. When the final mother liquor was examined it was found to consist of fairly pure yttrium chloride.

The first crystals which were precipitated were then further fractionated by dissolving in water containing a little hydrochloric acid, evaporating until rather thick, cooling by placing the container in snow and saturating with hydrogen chloride. The precipitated crystals were again dissolved in water and the same operations repeated several times. Since the chief interest lay in the least soluble portion, the mother liquors were placed aside each time. The following diagram shows the exact number of fractions that were taken.

Fraction 2e when dissolved in water showed very strong holmium bands while those of erbium could just be distinguished. The solution was precipitated by oxalic acid, the oxalate ignited to oxide and the equivalent determined.



The mother liquor 3h, which showed only a weak absorption of holmium, etc., was subjected to a double precipitation with oxalic acid. After ignition the equivalent of this fraction was also determined.

No. of Fraction.	I.	II.	Average	At. Wt.
2e	126.5	127.9	127.2	
3h	90.2	90.1	90.2	

Dennis and Dales<sup>1</sup> worked with the hydrogen chloride precipitation method for the fractionation of the yttrium earths. In this case a solution of  $MCl_3$  was concentrated and precipitated in ice-salt freezing mixture by passing in hydrogen chloride for 5 hours. The mother liquor was precipitated by ammonium hydroxide, dissolved in hydrochloric acid and again precipitated by hydrogen chloride. The original solution and the fractions were then compared as to spectra, and no change in the relative intensities of the spectra was observed. On this evidence Dennis and Dales rejected the method.

Since the use of hydrogen chloride is troublesome and unpleasant and moreover since the crystallization occurred mainly where the gas came in contact with the solution, it was thought that crystallization from 1:1 hydrochloric acid would be very much simpler and more effective.

All fractions except 2e and 3h from the preceding operations were combined, boiled down to hydrochloric acid of constant boiling point, and fractional crystallization was started. The solutions were evaporated until a scum formed on the surface, when they were allowed to stand for from 15 to 20 hours. Simple decantation was used instead of filtering and washing as was done with the hydrogen chloride method. By the time the tail fraction had become No. 9 the head fraction had become No. 4, owing to the combining of the small head fractions to obtain enough to work with. The atomic weights of these two fractions were then determined, and found to be 92.5 and 124.0, respectively.

<sup>1</sup> Dennis and Dales, *THIS JOURNAL*, 24, 421 (1902).

The crystals and mother liquor from Fraction 7 were next examined in order to find out the speed of separation given by one crystallization. The oxide from the crystals weighed 14.36 g. and the oxide from the mother liquor weighed 39.35. The atomic weight of the oxide from the crystals was found to be 106.1, while that from the mother liquor was 99.8.

After the above tests were made the fractionation was continued for 4 more operations, and the atomic weights of the extremes determined. The head fraction, No. 4, gave 133.70 while the tail fraction, No. 12 gave 91.5.

The absorption spectra were then examined by dissolving 1-g. portions of oxide from various fractions in equal amounts of nitric acid and diluting to the same volume in each case. Fraction 4 gave intense lines of holmium. The crystals from Fraction 7 gave fairly strong lines of holmium, while Fraction 12 gave only very faint lines of this element. Erbium was found to concentrate in the most soluble fractions with the yttrium. This indicated that erbium chloride was more soluble.

To follow the course of the small amount of dysprosium, Fraction 12 was concentrated and more of the solid was added until the holmium spectra in No. 4 and No. 12 were of about the same intensity. By comparing the intensity of the two faint dysprosium bands with that of the middle holmium band, it was estimated that in Fraction 12 the holmium band was 4 times as strong as the dysprosium bands, while in Fraction 4 the holmium was perhaps twice as strong as the two dysprosium bands. This indicated that relatively the dysprosium was twice as concentrated in No. 4 (the least soluble fraction) as it was in No. 12 (the most soluble fraction).

The order of separation in line of decreasing solubility of the chlorides would accordingly run: erbium, yttrium, holmium, dysprosium.

(c) **Basic Chlorides.**—In the case of the basic chloride, the crystals from Fraction 8 of the preceding experiment were dissolved in water, and ammonium hydroxide was added until a fair precipitate was obtained. The mixture was then heated and concentrated until the character of the hydroxide was changed into a granular basic chloride. Five fractions of about equal size were obtained, and of these Fraction 1 gave an atomic weight of 105.6 while Fraction 5 gave 93.4.

(d) **Basic Thiosulfates.**—These precipitates were obtained in the following manner. The boiling chloride solution was treated with very dil. ammonium hydroxide so long as the precipitated hydroxides would dissolve on continued boiling. A solution of sodium thiosulfate was then added, when the basic thiosulfates were immediately precipitated. The precipitate was filtered off, and the whole process repeated. Four fractions were obtained. The head fraction, No. 1, gave an atomic weight of 97.1, while the tail fraction, No. 4, gave 91.0,

### Summary.

The authors highly recommend the basic nitrate method in the two forms herein outlined for the separation of erbium, holmium, dysprosium and the less basic earths from yttrium; and the crystallization of the chlorides from 1:1 hydrochloric acid for the separation of holmium and dysprosium from yttrium.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY No. 366.]

## OXIDATION AND REDUCTION OF HYDROQUINONE AND QUINONE FROM THE STANDPOINT OF ELECTROMOTIVE-FORCE MEASUREMENTS.

By F. S. GRANGER AND J. M. NELSON.

Received October 23, 1920.

Very little work has been done on the study of oxidation and reduction from the standpoint of potential measurements, in the field of organic chemistry, and nearly all of that has been of an empirical character. Bancroft<sup>1</sup> included in a study of a large number of more or less common oxidizing and reducing agents, alkaline solutions of hydroquinone and pyrogallol. The proportions used in making up these solutions were not given, but had they been, they would not have thrown much light upon the composition of the resulting mixtures, since both hydroquinone and pyrogallol are very unstable in alkaline solutions. Furthermore, the potentials were not measured against any standard electrodes, but against other oxidizing and reducing agents. Neumann<sup>2</sup> later put Bancroft's results on a more definite basis by comparing them with a calomel electrode. Baur<sup>3</sup> determined the potentials manifested by solutions made up of definite amounts of hydroquinone and formaldehyde, in aqueous sodium hydroxide. Slaboszewicz<sup>4</sup> made some admittedly rough measurements on aldehyde and alcohol in 2*M* sulfuric acid. Mathews and Barmeier<sup>5</sup> published some potentials of various photographic developers and Frary and Neitz<sup>6</sup> carried out a more elaborate study along the same lines as those of Mathews and Barmeier. All of these measurements were determinations of potentials of solutions, made up with definite concen-

<sup>1</sup> Bancroft, *Z. physik. Chem.*, 10, 387 (1892).

<sup>2</sup> Neumann, *ibid.*, 14, 193 (1894).

<sup>3</sup> Baur, *Ber.*, 34, 3732 (1901).

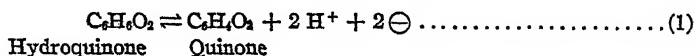
<sup>4</sup> Slaboszewicz, *Z. physik. Chem.*, 42, 343 (1902).

<sup>5</sup> Mathews and Barmeier, *Proc. 8th Intern. Congr. Appl. Chem.*, 20, 189, 193, 179 (1912).

<sup>6</sup> Frary and Neitz, *THIS JOURNAL*, 37, 2246 (1915).

trations of the components but without any reference to the reaction taking place or the products formed, so that the results, while interesting in some cases from the technical side in showing the reducing powers of these particular solutions, are still of little scientific significance.

Haber and Russ<sup>7</sup> in a study of the electrolytic reduction of some organic compounds, such as nitrobenzene and quinone, observed that when the potential of a platinum electrode immersed in a quinone-hydroquinone solution was measured against a calomel electrode it behaved similarly to an ordinary metal electrode immersed in a solution of one of its salts. They considered the reaction which takes place in the quinone-hydroquinone solution to be



and compared the difference in the observed potentials of any two solutions with the corresponding difference in calculated values, obtained by means of Equation 3

$$\pi_1 - \pi_2 = \frac{RT}{2F} \left[ \ln \frac{(\text{Quinone})}{(\text{Hydroquinone})_1} - \ln \frac{(\text{Quinone})_2}{(\text{Hydroquinone})_2} \right]. \quad (3)$$

Equation 3 is the usual van't Hoff Equation 2

$$\pi = \frac{RT}{2F} \left[ \ln \frac{\text{Quinone} \times [\text{H}^+]^2}{\text{Hydroquinone}} - \ln K \right] \quad (2)$$

so modified as to avoid taking into account in the calculations the acidity of the solutions. This is of course possible by keeping the acidity the same in all the experiments. They found that the calculated and observed differences, obtained in this way, agreed quite well. Due to this agreement they concluded that the van't Hoff Equation 2 was applicable, and that this organic reaction was similar in character to oxidation-reduction reactions occurring in the case of electrolytes.

As is well known, quinone and hydroquinone combine, reversibly, in solution to form quinhydrone, and as no data as to the extent of this combination were at hand the actual or relative concentrations of quinone and hydroquinone in Haber and Russ's solutions, which were prepared by adding known excesses of either one of these substances to a solution of quinhydrone, were unknown and undetermined. There exists, therefore, one important assumption in their method of reasoning which requires additional experimental data before it can be considered as justified. Haber and Russ assumed on the one hand, that the van't Hoff equation was applicable and therefore the quinhydrone must have been practically completely dissociated, and on the other hand, that since the quin-

<sup>7</sup> Haber and Russ, *Z. physik. Chem.*, 47, 257 (1904).

hydrone was completely dissociated and therefore the concentrations of quinone and hydroquinone known, the van't Hoff equation was applicable.

In the present investigation the determination of the actual concentrations of the reactants was undertaken and the study was extended to varying hydrogen-ion concentration as well. By the use of the data obtained it has been possible to show, without resorting to any assumption as to the degree of the dissociation of the quinhydrone as Haber and Russ did, that the calculated values, using Equation 3, for the differences in the electromotive-force measurements of any two solutions of different concentrations of quinone and hydroquinone, agree with the corresponding experimental values. Furthermore, having determined the actual concentrations of the reactants, quinone, hydroquinone and hydrogen ion, it has been possible to calculate also, by means of Equation 2, the potential of each solution and to show that this calculated value agrees with the experimental value, when the difficulties in determining the exact concentrations of the reactants and resultants of the reaction are taken into consideration and when it is borne in mind that the van't Hoff equation is based on the ideal gas laws and osmotic pressure rather than upon concentration. This method is therefore more satisfactory and direct for ascertaining the applicability of the van't Hoff equation than that of only comparing the differences between the potentials of two solutions with the corresponding calculated values.

### Determination of the Concentrations of the Reactants and Resultants.

**Solubility of Hydroquinone.**—Since no data on the solubility of hydroquinone at 25° could be found in the literature, solubility determinations were made.

TABLE I.

G. per 100 cc. of Solution.

Solvent.	1.	2.	3.	4.	5.	Av.	Moles per liter.
Water.....	7.094	7.091	7.112	7.086	...	7.10	0.645
0.01M HCl.....	7.060	7.128	7.136	7.028	7.146	7.10	0.645
0.1 M HCl.....	6.978	6.944	...	...	...	6.96	0.633
1.0 M HCl.....	5.436	5.442	...	...	...	5.44	0.494

Because the hydrogen ion is considered as one of the resultants in the reaction, Equation 1, various amounts of hydrochloric acid were added. The hydrochloric acid also served to make the solutions good conductors, which of course is necessary. It will be noticed in the table that the hydrochloric acid decreased the solubility of the hydroquinone.

**Solubility of Quinone.**—The solubility of quinone in water at 25° had been determined previously by Luther and Leubner<sup>8</sup> using the analytical method of Valeur<sup>9</sup> which consisted in titrating the liberated iodine with thiosulfate. In this way they found the solubility of quinone to be 1.265 moles per liter, a value in which there is evidently an

<sup>8</sup> Luther and Leubner, *J. prakt. Chem.*, 85, 314 (1912).

<sup>9</sup> Valeur, *Compt. rend.*, 129, 552 (1899).

TABLE II.

Solvent.	Moles per liter.		G. per 100 cc.
	1.	2.	
Water.....	0.1266	0.1266	1.37
0.1 <i>M</i> HCl.....	0.1275	0.1275	1.38
1.0 <i>M</i> HCl.....	0.1332	0.1332	1.44

error in the placing of the decimal, since the value we obtained by repeating the determination is just one-tenth of theirs.

Here again it is to be noticed that the hydrochloric acid influences the solubility, but in the opposite direction from that observed in the case of hydroquinone.

**Solubility of Hydroquinone and Quinone in the Presence of Each Other.** Solubility of Quinhydrone.—It was not possible to make up solutions containing known concentrations of both hydroquinone and quinone by simply dissolving weighed quantities of these substances in a measured volume, because they combine immediately in equimolar proportions to form quinhydrone. Furthermore, since in solution the quinhydrone exists in mobile equilibrium with them their concentrations cannot be determined directly, by analytical means. For the series of solutions (see below), in which only the hydrogen-ion concentration varied, the concentrations of either hydroquinone or quinone were fixed by saturating the solutions with one of them and quinhydrone. A solution saturated with both was not possible owing to the slight solubility of the quinhydrone, which separated out when only a small quantity of quinone was added.

In order to prepare solutions containing known concentrations of the reactants it was necessary to know not only their solubilities and that of quinhydrone but also the degree of dissociation of the latter into its components, hydroquinone and quinone.

Luther and Leubner determined the solubility, in water, of the undissociated quinhydrone and also its dissociation constant by a method similar to that used by von Behrend<sup>10</sup> for the phenanthrene picrates. They saturated water and aqueous hydroquinone solutions of known concentrations with quinhydrone at 25°, and determined the total quinone, combined and free, present in the filtrate by Valeur's method, which is applicable owing to the complete dissociation of the quinhydrone as the quinone is removed by the iodide. This total quinone represents (formula-weight for formula-weight) the total quinhydrone, dissociated and undissociated, which was dissolved in saturating the solution. If *s* is the solubility of the undissociated quinhydrone, *a* the solubility of the undissociated and dissociated quinhydrone, *b* the known excess of hydroquinone added, *h* the actual concentration of hydroquinone, *q* the actual concentration of quinone, all in formula-weights per liter, then the free and combined hydroquinone in the solution, which is the same in moles as the total quinhydrone (dissociated and undissociated) or *a*, plus the added excess of hydroquinone, *b*, is equal to the hydroquinone combined in the undissociated quinhydrone, *s*, plus the free hydroquinone, *h*, in the solution; or

$$a + b = s + h; \text{ or } h = a + b - s \quad (4) \text{ and } (5)$$

The total quinone (free and combined in the form of quinhydrone) in the solution, *a*, determined by titration, is equal to the undissociated quinhydrone, *s*, plus the free quinone, *q*; or

$$a = s + q; \text{ or } q = a - s \quad (6) \text{ and } (7)$$

<sup>10</sup> von Behrend, *Z. physik. Chem.*, 15, 183 (1894).



The dissociation constant,  $K$ , of the quinhydrone, assuming that the mass law holds in this case, can be represented as

$$K = (q \times h)/s; \text{ or } Ks = q \times h \quad (8)$$

Substituting in (8) the values for  $q$  and  $h$ , from Equations 7 and 5 respectively, then

$$Ks = (a - s)(a + b - s) \quad (9)$$

If the experimental precision were fine enough,  $s$ , and  $K$ , in Equation 9, could be calculated from any pair of determinations by means of simultaneous equations, since  $a$  and  $b$  are measured quantities. But comparatively slight deviations from these ideal conditions render this method of calculation inapplicable, so that recourse must be had to a method of trial and approximation which Luther and Leubner carried out in the following way.

By trying different values for  $s$  in Equation 9, they found  $K$  to approach the nearest to constancy when  $s$  was assigned the value 0.0013.

TABLE III. (Luther and Leubner.)

Added hydroquinone $b$ .	Solubility of quinhydrone $a$ (Av.)	$a - b$ .	$K(s = 0.0013)$ .
0.0	0.01827	0.01827	0.221
0.01	0.01421	0.02421	0.227
0.02	0.01150	0.03150	0.236
0.05	0.00664	0.05664	0.227

Luther and Leubner's determinations were repeated in this work and the range extended up to the saturation point for hydroquinone in water, and also in 0.1 molar and molar hydrochloric acid. The results are given in Table IV.

TABLE IV.

Moles per liter.			Solvent, water and no hydrochloric acid. Dissociation constant, $K \times 10^3$ , for quinhydrone when $s$ (moles per liter of undissociated quinhydrone) has the following values.						
Added hydroquinone $b$ .	Quinhydrone (dissoc. and undissoc.) $a$ .	Total hydroquinone $a + b$ .	$s =$	0.0013	0.00125	0.00100	0.00098	0.00096	0.00095
0.0	0.0178	0.0178	209	219	282	289	296	299	
0.01	0.0135	0.0235	208	218	282	289	295	298	
0.02	0.0106	0.0306	210	219	284	291	298	301	
0.05	0.00625	0.05625	210	220	290	297	304	308	
0.1	0.00374	0.10374	192	204	282	290	298	302	
0.2	0.00244	0.20244	176	192	290	300	310	316	
0.3	0.00189	0.30189	136	154	268	280	292	298	
0.4	0.00179	0.40179	152	178	316	332	347	355	
0.5	0.00172	0.50172	162	189	361	378	397	405	
Sat'd	0.001815	0.645 - $s$	255	291	526	550	574	587	
Mean of the first 7 values.			192	204	283	291	299	303	
Sum of deviations from mean.			141	122	33	31	32	35	

TABLE IV (Continued).

Solvent, 0.1 M hydrochloric acid.					
<i>b.</i>	<i>a.</i>	<i>a + b.</i>	<i>s</i> = 0.00103	0.00102.	0.00101
0.000	0.0173	0.0173	256	260	263
0.01	0.0131	0.0231	259	262	264
0.02	0.0102	0.0302	259	263	265
0.05	0.00593	0.05593	261	264	267
0.1	0.00363	0.10363	259	263	265
0.2	0.00237	0.20237	262	267	271
0.3	0.00190	0.30190	254	260	265
0.4	0.00172	0.40172	268	274	281
0.5	0.00170	0.50170	326	334	342
Sat'd	0.00181	0.633 + <i>s</i>	478	490	501
Mean of first 7 values.			289	263	264
Sum of deviation from mean.			13	12	14

Solvent, Molar hydrochloric acid.					
<i>b.</i>	<i>a.</i>	<i>a + b.</i>	<i>s</i> = 0.00098.	0.00087.	0.00086.
0.0	0.0162	0.0162	267	270	274
0.01	0.0118	0.0218	260	263	267
0.02	0.0091	0.0291	264	267	270
0.05	0.0052	0.0552	267	270	274
0.1	0.0031	0.1031	258	262	266
0.2	0.00202	0.20202	261	267	272
0.3	0.00164	0.30164	260	267	273
0.4	0.00152	0.40152	291	299	307
Sat'd	0.00159	0.494 + <i>s</i>	399	409	419
Mean of first 7 values.			262	266	271
Sum of deviations from mean.			21	18	19

On comparing the values obtained in the case of the water solution with those of Luther and Leubner, it will be seen that the values for *a*, the solubility of quinhydrone (dissociated and undissociated), are lower than theirs by about 5%. The reason for this latter difference has not been ascertained. The selected value for *s*, the solubility of the undissociated quinhydrone, which gives the minimum sum of deviations for the dissociation constant, *K*, from its mean, for the range comprising the first four solutions, which was as far as the determinations of Luther and Leubner were carried, is 0.00125 formula-weights per liter, which is a very close agreement with theirs. If, however, the entire range, up to the saturation point of hydroquinone, is considered it will be seen that in the column under *s* = 0.00125, there is a decided but continuous decrease in the value for *K*, until the added hydroquinone amount to *b* = 0.3 mole per liter, and after that a gradual increase occurs which becomes suddenly abrupt at the saturation point of the hydroquinone.

When the smaller values for the solubility of the undissociated quinhydrone, *s*, are considered, it is seen that the first 7 values of the dissociation constant, *K*, in their respective columns become more uniform, giving a minimum deviation sum of 31 for *s* = 0.00098. This latter value for *s* was selected as the solubility, formula weight per liter, in preference to the value, *s* = 0.0013, originally put forth by Luther and Leubner.

Parallel results were obtained with 0.1 and 1 M hydrochloric acid solutions. The calculated solubilities and the dissociation constants for the quinhydrone are recapitulated in Table V. The basis of the last column is given in the subsequent part of the paper.

TABLE V.

Solvent.	Mole of quinhydrone per liter.		Dissociation constant, <i>K</i> for quinhydrone.	
	Sol. of quinhydrone (dissoc. and undissoc.).	Sol. of quinhydrone (undissociated).	(Av. first 7).	When solution was satur. with hydroquinone.
	<i>a</i> .	<i>s</i> .		
Water.....	0.0178	0.00098	0.289	0.550
0.1 <i>M</i> HCl.....	0.0173	0.00102	0.263	0.490
1.0 <i>M</i> HCl.....	0.0162	0.00087	0.267	0.409

### Determination of the Hydrogen-Ion Concentration, or the Acidity of the Solutions.

One of the difficulties encountered in this work was the determination of the hydrogen-ion concentration of the various solutions studied. In the case of the acid solutions conductivity data were used for this purpose. This involved, of course, the tentative assumption that the condition of the acid, or hydrogen-ion concentration, was the same as in a pure solution of hydrochloric acid. The question naturally arises, why not determine the hydrogen-ion concentration by the electromotive-force method with a hydrogen electrode. This method was not used at all (although it was realized that the assumption upon which the use of the conductivity values was based, might be the source of considerable error), because it was believed that, even if a constant potential could be obtained with a hydrogen electrode, in the presence of another active electrochemical system this potential still might be very different from the true hydrogen-ion potential because of the influence of the other system. It was felt that this was too big a question to take up in the time at our disposal.

For this reason, the values for the hydrogen-ion concentrations were obtained as follows. Bray and Hunt<sup>11</sup> by the conductivity method, found for the degree of ionization ( $\alpha$ ) of hydrochloric acid at 25°, 92.1% in 0.1*M* solution, and 97.1% in 0.091*M* solution. But no direct data could be found in the literature for 0.1*M* hydrochloric acid at 25°. Kohlrausch,<sup>12</sup> however, gives the following for the equivalent conductivity ( $\Lambda$ ) at 18°:

Moles per liter.	$\Lambda$ .
0.01	370
0.1	351
1.0	301

From these figures  $\Lambda_{.1}/\Lambda_{.01}$  is found to be 0.948 at 18°, while from Bray and Hunt's data  $\alpha_{.1}/\alpha_{.01}$  is found to be 0.948 at 25°. Moreover, according to Kohlrausch,<sup>13</sup> the temperature coefficient of conductivity of

<sup>11</sup> Bray and Hunt, *THIS JOURNAL*, 33, 781 (1911).

<sup>12</sup> Landolt-Börnstein, "Tabellen," 1912, p. 1104.

<sup>13</sup> *Op. cit.* p. 1115.

comparatively constant by saturating the solutions with either hydroquinone or quinone, and with quinhydrone, while the hydrogen ion or acidity varied. The values for the observed potentials of the solutions A, B and C, were obtained by averaging all of the measurements taken on a given mixture during the period in which the readings produced practically a horizontal line. These values are given in Table IX.

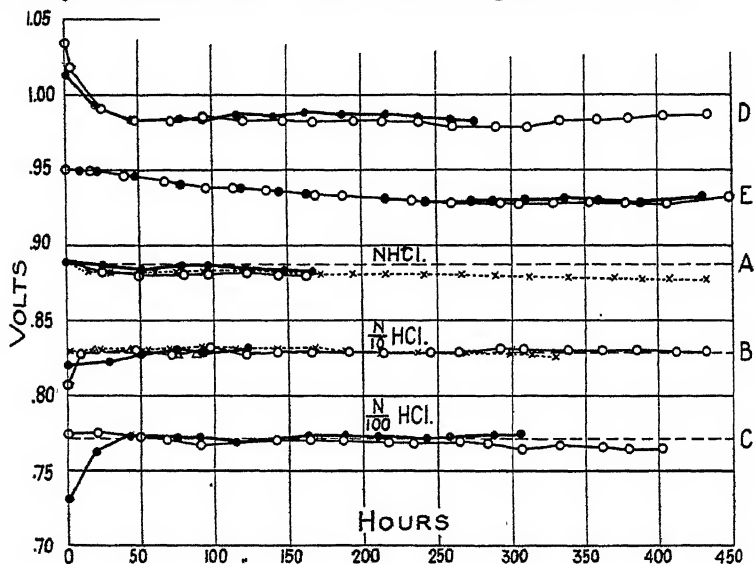


Fig. 2.

**Agreement Between the Calculated and Observed Potentials of the solutions, Containing Known Concentrations of Quinone, Hydroquinone and Acid.**—In Table VI is given a comparison between the calculated and observed differences in potentials,  $\pi_1 - \pi_2$ , manifested by different

TABLE VI.

Solution.	$b$ .	$q = a - s$ .	$h = a + b - s$ .	$\pi_1 - \pi_2$	
				Calc.	Obs.
J	0.0	0.01628	0.01628	0.00781	0.0075
I	0.01	0.01208	0.02208		
H	0.02	0.00918	0.02918	0.00741	0.0065
G	0.05	0.00491	0.05491		
F	0.10	0.00261	0.10261	0.0162	0.0155
				0.0163	0.0165

pairs of the solutions, F, G, H, I and J. All of these measurements were done at 25° and in 0.1M hydrochloric acid solutions and therefore Equation 3 above can be written

$$\pi_1 - \pi_2 = 0.0298 \log q_1/h_1 - 0.0298 \log q_2/h_2. \quad (3)$$

The values for  $h$ , the concentration of hydroquinone,  $q$ , the concentration of quinone, in the above solutions, were obtained from the values of  $a$ , the concentration of quinhydrone (dissociated and undissociated) present in the solutions,  $s$ , the concentration of the undissociated quinhydrone, and  $b$ , the amount of added hydroquinone, all of which are given in Table IV. The values of  $b$  are given also in the description of the solutions.

As can be seen in Table VI, the calculated values for the differences in potentials,  $\pi_1 - \pi_2$ , agree quite well with the observed values, and therefore are like those obtained by Haber and Russ. They have, however, the additional weight over the values of Haber and Russ in that they are based on determined concentrations of quinone and hydroquinone instead of assumed values.

**The Solubility of the Undissociated Quinhydrone is Independent of the Presence of an Excess of Hydroquinone.**—It was pointed out in the discussion following Table IV that there is an abrupt increase in the values of the dissociation constant,  $K$ , of the quinhydrone as the solutions become saturated with respect to hydroquinone. Due to the method of trial and Equation 9 used in obtaining the values of  $K$  in Table IV, the assumption was made that the solubility of the quinhydrone,  $s$ , was not affected by the varying concentration of hydroquinone present in the solutions. Some evidence for the justification of this assumption can be had by comparing the potentials of Solutions F to J, which were not saturated with hydroquinone, with the potentials of Solutions A, B and C, which were. It is not extravagant to assume that Solutions A, B and C obey the van't Hoff equation just as Solutions F to J do, since when compared with the latter in this respect (see Table IX below) their potentials appear to be normal.

Solution B has the same acidity as Solutions F to J, and therefore it is possible by means of Equation 3

$$\pi_1 - \pi_2 = 0.0298 \log (q/h)_1 - 0.0298 \log (q/h)_2 \quad (3)$$

to obtain an expression involving only the one unknown  $(q/h)_2$ , since  $(q/h)_1$  is given in Table VI and the potentials,  $\pi$ , can be obtained from the graphs. Inspection of Fig. 1 shows that Solution F gives a very stable potential. Therefore the data for this solution were selected as the basis of this calculation, taking for  $\pi_F$ , the initial reading, 0.8695 volt, obtained as explained above, and which is also the average of the readings up to the point at which the falling off commences. Similarly Solution B, Fig. 2, has an average value for  $\pi_B$  of 0.8300 volt. Introducing these values and also  $-0.0475$  for  $0.0298 \log (q/h)_F$ , from Table VI, in Equation 3

$$0.8695 - 0.8300 = -0.0475 - 0.0298 \log (q/h)_B \text{ or } (q/h)_B = 0.001202.$$

But  $h_B$ , the concentration of hydroquinone in 0.1M hydrochloric acid

is 0.633 mole per liter (Table I) and therefore  $q_B$ , the concentration of the quinone in Solution B is 0.00076 mole.

Since Solution B was saturated with hydroquinone and quinhydrone, the total quinhydrone (dissociated and undissociated), present in the solution, and  $a_B$  is 0.00181 mole (Table IV), is equal to the undissociated quinhydrone  $s_B$  plus the concentration of the free quinone  $q_B$  is 0.00076 mole, because the number of moles of the latter is equivalent to that of the dissociated quinhydrone in this case since no quinone had been added to the solution. Then from

$$a_B = s_B + q_B \dots \dots \dots (6)$$

the solubility  $s_B$  of the undissociated quinhydrone in Solution B is 0.00105 mole per liter. This value is so close to 0.00102, the value assumed in Table IV, that the assumption mentioned above appears to be justified.

Instead of using Solution F for this purpose, the other solutions, G, H, I and J, were tried also and gave the following results:

Basis.	$s_B$ .
F	0.00105
G	0.00105
H	0.00101
I	0.00094
J	0.00092

The values obtained when Solutions I and J were used as the basis for the calculations of the concentration of the undissociated quinhydrone,  $s_B$ , are slightly lower. The higher values from Solutions F, G and H are to be preferred because these solutions manifested more stable and definite potentials, as is evident from our examination of the corresponding curves, especially those of F and G in Figs. 1 and 2.

**Calculation of Potentials of Solutions, Saturated with Hydroquinone and of Various Acidities.**—Adopting, for the reasons just stated above the values for  $s$ , the solubility of the undissociated quinhydrone showing the smallest deviation from the mean, and given in Table IV, it becomes possible to calculate the potentials of Solutions A, B and C. The procedure followed in these calculations differs from that in the case of Solutions F to J, in that the acidity of the solutions varied and therefore had to be taken into account in Equation 3, or

$$\pi_1 - \pi_2 = 0.0298 \log(q/h)_1 + 0.0596 \log[H^+]_1 - 0.0298 \log(q/h)_2 - 0.0596 \log H^+_2 \quad (10)$$

The values of the hydrogen-ion concentrations are given in the section dealing with the concentration of hydrogen ion. The values of  $q$ , the concentration of the free quinone, are obtained by means of Equation 6, and since the solutions were saturated with respect to hydroquinone, the value of  $h$  is given in Table I. The values for  $a$ , the total concentration

of quinhydrone (dissociated and undissociated) and  $s$ , the concentration of the undissociated quinhydrone, are given in Table IV. The value of  $s$  for Solution C, which was 0.001  $M$  with respect to hydrochloric acid, is considered to be the same as that for pure water. No solubility experiments for 0.01  $M$  hydrochloric acid solutions were run because the results obtained for 0.1  $M$  hydrochloric acid and water were so nearly the same that these determinations for 0.01  $M$  hydrochloric acid seemed unnecessary. The results obtained are given in Table VII.

TABLE VII.

Solution.	$\frac{q}{a-s}$	$h$	$H^+$	$\pi_1 - \pi_2$ Calc.	$\pi$ Obs.	$\pi_1 - \pi_2$ Obs.
A	0.00072	0.494	0.790	0.0579	0.883	0.053
B	0.00079	0.633	0.0921		0.830	
C	0.000835	0.645	0.00971	0.0576	0.770	0.060

In like manner,  $\pi_A - \pi_C = 0.1155$  (calc.) and 0.113 (observed). Thus the observed potentials are found to agree quite well with the theoretical, just as was found to be the case for Solutions F to J, even though in these solutions the concentration of the hydrogen ion was varied.

**The Equilibrium Constant of the Oxidation-Reduction Reaction between Quinone and Hydroquinone.**—The value of the equilibrium constant, for the oxidation-reduction reaction (1) between quinone and hydroquinone,  $K$ , was obtained by means of Equation 2.

$$\pi = 0.0298 \log(q/h) + 0.0596 \log[H^+] - 0.0298 \log K \dots \dots (2)$$

The concentrations of the free quinone and hydroquinone,  $q$  and  $h$ , were taken from Tables VI and VII. The hydrogen-ion concentration can be found in the section dealing with the concentration of hydrogen ion. In Table VIII are given the values for  $K$ , obtained in the form  $0.0298 \log K$ .

TABLE VIII.

Solution.	A.	B.	C.	F.	G.	H.	I.	J.
$-0.0596 \log H^+$	0.0061	0.0618	0.1200	0.0618	0.0618	0.0618	0.0618	0.0618
$\pi$	0.8830	0.8300	0.7700	0.8695	0.8860	0.9015	0.9075	0.9150
$-0.0298 \log(qh)$	0.0845	0.0867	0.0861	0.0475	0.0312	0.0149	0.0078	0.0000
$0.0298 \log K$	-0.9736	0.9785	0.9761	0.9788	0.9790	0.9782	0.9771	0.9768
Deviation	-0.0037	+0.0012	-0.0012	+0.0015	+0.0017	+0.0009	-0.0002	-0.0005

The mean value for  $0.0298 \log K$  is 0.9773, and hence the equilibrium constant for Reaction 1 is  $K = 1.6 \times 10^{-23}$ .

The average deviation in the values for  $0.0298 \log K$ , as can be seen in Table VIII, is 0.0014 volt or 1.4 millivolts. This compares favorably with the closest agreement that has been obtained in parallel work in inorganic chemistry, as can be seen from the following summary.

System.	Investigators.	Average dev. millivolts.
Ferrous/ferric	Peters(Tab. 1)	3.9
" "	" "	2.7
Ferrocyanide/ferricyanide	Friedenhagen	1.0
Manganate/permanganate	"	4.0
Uranous/uranyl	Luther and Michie	1.2
Iodine/iodate	Luther and Sammet	0.8
Bromine/bromate	" "	1.0
Bromide/bromine	" "	0.5
Iodide/iodine	" "	1.0
Hydroquinone/quinone	This work	1.4

### Comparison of the Theoretical and Observed Potentials.

By using the mean value, obtained above for  $0.0298 \log K = 0.9773$  the theoretical values for the potentials of the various solutions have been calculated and arranged together with the observed values in Table IX for the sake of comparison.

TABLE IX.

Solution	$\pi$ (Calculated).	$\pi$ (Observed).
A	0.8867	0.8830
B	0.8288	0.8300
C	0.7712	0.7700
F	0.8680	0.8695
G	0.8843	0.8860
H	0.9006	0.9015
I	0.9077	0.9075
J	0.9155	0.9150

The theoretical potentials are represented in the figures by the straight dotted lines.

**Potential Measurements on Unstable Solutions.**—Seven cells saturated with quinone and a great number of neutral and alkaline solutions, in which potassium chloride and sodium hydroxide were used as electrolytes, were run also. Full details on these measurements are given in the original dissertation.<sup>14</sup> They are omitted here, for the reason that on account of the extreme instability of these solutions they could not be made the basis of any quantitative calculations.

Qualitatively, however, they were perfectly in accord with the theory. The solutions saturated with quinone, as already shown, gave higher oxidizing potentials than solutions of the same acidity, but of lower ratio between the quinone and the hydroquinone,  $q/h$ . The neutral solutions gave lower potentials than the acid solutions, and the alkaline gave still lower potentials, decreasing as the alkalinity was increased.

<sup>14</sup> "Oxidation and Reduction in Organic Chemistry from the Standpoint of Potential Differences," by F. S. Granger. Columbia University Press, New York, N. Y., 1920.



### Experimental Part.

**Hydroquinone.**—The hydroquinone used was partly Merck's and partly Eimer and Amend's. Only one grade was obtainable and it was claimed to be very pure. No accurate method for determining its purity could be found. It all melted at  $169^{\circ}$  (uncorrected), the same value as given by Hlasiwetz,<sup>15</sup> or  $173.0^{\circ}$  (corrected). The solubility determinations of the hydroquinone were made by evaporating 5 cc. of a saturated solution to constant weight in weighed flasks, at room temperature and about 25 mm. pressure.

**Quinone.**—The quinone was Kahlbaum's. Some of it was recrystallized from gasoline (which was found to be an excellent solvent for this purpose). Both methods gave clean, bright yellow products, titrating, by the method already described, 99.4% of the theoretical requirement, and melting sharply at  $115.7^{\circ}$  (corrected), the melting point given in Beilstein.

**Quinhydrone.**—The quinhydrone was prepared in two ways: by treating an aqueous solution of hydroquinone with ferric chloride, and then acidifying with hydrochloric acid; and by mixing equivalent amounts of hydroquinone and quinone in water. The product, in each case, was filtered off and washed with water. That by the first process titrated 99.2% of the theoretical amount by the method previously described. Some was recrystallized from alcohol followed by ether, and some from glacial acetic acid. Acetic acid proved to be a very good solvent for the purpose, being by far the best of the three. All of the recrystallized products titrated 99.4%. Only the samples giving this titration were used. Quinhydrone decomposes upon heating, so its purity can not be checked in this way.

In determining the solubility of the quinhydrone, solutions containing an excess of the material were placed in a large test-tube fitted with a spiral mechanical stirrer, immersed in the thermostat, and vigorously and continuously stirred. Samples were taken out every 15 to 30 minutes, by means of a pipet fitted with a filter, until two successive titrations gave the same value, which was usually the case with the first two samples. In a number of cases, fresh mixtures were made up and tested as checks, and all the results were almost identical with the original, so it was not deemed necessary to verify all the solutions in this way, the regularity of the results and the parallelism between the aqueous and acid solutions also serving as a check.

**Potential Measurements.**—Sensitive Leeds and Northrup potentiometer and galvanometer were used. Saturated potassium chloride solution was used as the connecting medium. The cells were kept immersed in a constant temperature bath at  $25^{\circ}$ , the temperature remaining constant to  $0.01^{\circ}$ . Nitrogen was bubbled through the solution in the cell, for the first few hours, to insure complete removal of the air and to provide agitation at the start. The gas inlet and outlet tubes were closed then to prevent access of air. The potential of each cell was measured at least once a day over a period of from one to three weeks. Two or more cells of each solution were made up and examined, usually at different times and sometimes with different lots of materials, in order to determine the reproducibility of the potentials measured. No marked difference was observed, whether the electrodes were platinized or not.

The authors wish to express their appreciation to the Harriman Research Laboratory for aid in this investigation.

NEW YORK, N. Y.

<sup>15</sup> Hlasiwetz, *Ann.*, 177, 336 (1875).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 361.]

THE FACTORS AFFECTING THE STABILITY OF ADDITION COMPOUNDS IN SOLUTION AND THEIR INFLUENCE UPON IONIZATION EQUILIBRIA (Part I).<sup>1</sup>

BY JAMES KENDALL AND PAUL M. GROSS.

Received January 11, 1921.

It is unfortunate that any attempt to modify the currently accepted ionization theory inevitably introduces a great many complicating factors, especially when solutions of finite concentration are considered. Compound formation between solvent and solute, changes in molecular complexity of solvent and solute, complex ion formation, etc.—all these are influences about which so little is definitely known that it soon becomes impossible to treat the subject satisfactorily in a strictly quantitative manner. Before any real advances can be made toward a new and more comprehensive theory it will consequently be necessary to examine very closely the effect of these various factors upon the simple equilibrium postulated at present between “ionized” and “non-ionized” solute.

Some preliminary steps in this direction have been made in earlier

<sup>1</sup> This article was practically completed in 1917 (see Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2303 (1917)); its publication has been delayed by the absence of both authors on war work and by the subsequent postponement of the additional experimental tests which it was desired to impose upon the views here put forward. The first section of this confirmatory experimental work is now presented in the succeeding article.

In the interim, many investigators in this field have followed Milner, (*Phil. Mag.*, 35, 214 and 354 (1918)) and Ghosh (*J. Chem. Soc.*, 113, 449 and 627 (1918)) in postulating complete ionization in solutions of strong electrolytes. Mention may be made in particular of recent articles by A. A. Noyes and MacInnes (*THIS JOURNAL*, 42, 239 (1920)), and by Langmuir (*ibid.*, 42, 287 (1920)). The whole question of the abnormality of strong electrolytes, as related to the ionization hypothesis advanced in this and previous papers, will be dealt with in detail in a subsequent article of this series, so that it would be premature to dwell upon the matter at this point. As may be gathered from the contents of this communication, however, the present authors are not in agreement with the fundamental assumption of Ghosh that the *only* equilibrium to be considered in a solution of a strong electrolyte  $RX$  in water is the electrostatic equilibrium between simple “free” and “bound” ions  $R^+$  and  $X^-$ , but insist upon the additional necessity of taking into account the existence of solvent-solute complexes in all conducting solutions and their influence upon ionization. Inter-ionic attractive forces must undoubtedly be recognized in any final quantitative treatment of the problem, but no satisfactory solution can possibly be obtained if all other factors are totally neglected. In this connection it may be profitable to repeat the opinion clearly expressed in a recent paper by Wells and Smith (*THIS JOURNAL*, 42, 185 (1920); see also previous articles by G. McP. Smith in *ibid.*) that our failure to elucidate ionization equilibria has been mainly due to our refusal to take into account the occurrence of complex chemical reactions between the different ionic and molecular species in the solution. The factors affecting such reactions are further discussed in the present communication.

articles of this series.<sup>2</sup> The basis of the hypothesis there advanced is that ionization in solution is preceded by the formation of solvent-solute complexes, and that the disintegration of these into ions of opposite charge results from the diminished electrostatic attraction between the constituent radicals. The extent of ionization in any solution will consequently depend upon (a) the extent of compound formation; *i. e.*, the degree to which reactions of the type  $AB + CD \rightleftharpoons AB \cdot CD$ <sup>3</sup> proceed from left to right in a mixture of AB and CD in the liquid state; and (b) the extent of the dissociation of these compounds into ions of opposite charge; *i. e.*, the degree to which reactions of the type  $AB \cdot CD \rightleftharpoons A^+ + (B \cdot CD)^-$  proceed from left to right in the same mixture.

If the amount of compound formation is large and if these compounds are, ionically, extremely unstable, then the solution will exhibit a high conductivity. On the other hand, where there is little combination or where the compounds formed are comparatively stable ionically, the conductivity of the mixture can be but small.

We shall therefore be able to *predict* the extent of ionization in any solution when we have once established what factors affect the formation and the ionic stability of solvent-solute complexes in general. The first half of this problem has already been discussed,<sup>4</sup> and it has been demonstrated experimentally that the extent of formation of addition compounds between solvent and solute (in other words the stability of complexes *with respect to their components*) increases uniformly with the differences in character (*i. e.*, in the positive or negative nature of the constituent groups) of these components. It is particularly noteworthy that complexes other than the simplest possible type  $AB \cdot CD$  are formed in quantity only when AB and CD are decidedly diverse.

In the present article the study of the second half of the problem—the factors affecting the stability of solvent-solute complexes *with respect to their ionic dissociation products*—is initiated. In their simplest form<sup>5</sup>

<sup>2</sup> Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2303 (1917); Kendall and Booge, *ibid.*, 39, 2323 (1917). These articles also give references to the extensive work of previous investigators upon various aspects of the problem. Two typographical errors in the equations given in the former paper may be corrected here. On p. 2309, read  $1/T_0$  instead of  $T_0$  in Equation 2. On p. 2313, read 1200 *c* instead of 12000 calories in the equation on line 9.

<sup>3</sup> In the first articles of this series (*e. g.*, Kendall, *THIS JOURNAL*, 36, 1242 (1914)) the mechanism of this type of reaction was discussed in a very inadequate manner, an ionic basis being postulated. However, as has been pointed out by Dehn (*ibid.*, 39, 2647 (1917)), a reaction is not necessarily ionic because it is instantaneous. A more logical view has been briefly outlined in a later article (Kendall and Booge, *ibid.*, 39, 2328 (1917)), and in favor of this view the earlier argument may now be definitely discarded.

<sup>4</sup> For a résumé see Kendall, Booge and Andrews, *loc. cit.*, p. 2304.

<sup>5</sup> The arguments which follow immediately below are independent of the actual formula of the complex or of its mode of ionization.

the reactions here involved may be written,  $AB \cdot CD \rightleftharpoons A^+ + (B \cdot CD)^-$ . The case where AB and CD are identical molecules (or  $AB \cdot CD$  is an associated pure liquid) may first be briefly considered.

### The Ionization of Pure Liquids.

Any liquid, the simple molecules of which contain unsaturated atoms, will exhibit to a greater or less degree the phenomenon of association.<sup>6</sup> As a consequence of this association, the moments of the electrical doublets present in the simple molecules are considerably increased, and the constraints upon the electrons correspondingly diminished. The higher the degree of association, therefore, the less firmly are the constituent groups of the complex molecules held together, and the more readily will disintegration into ions of opposite charge take place. We should expect, then, that self ionization is in general a property *characteristic of highly associated liquids*. In a series of liquids of similar type, arranged in order of ascending molecular complexity, a regular increase in specific conductivity should be apparent.<sup>7</sup>

Such is in fact the case. Ideal non-associated liquids (such as the saturated hydrocarbons) possess practically zero conductivity.<sup>8</sup> Other normal organic substances (for example, benzene, chloroform, ether) are extremely poor conductors, the specific conductivity at 25° being of the order  $10^{-4}$ . When we examine the associated organic liquids,<sup>9</sup> somewhat higher values are recorded in the literature: *e. g.*, formamide,  $\kappa_{25^\circ} = 4.7 \times 10^{-5}$ ; acetone,  $\kappa_{25^\circ} = 2.27 \times 10^{-7}$ ; formic acid,  $\kappa_{25^\circ} = 6 \times 10^{-6}$ ; methyl alcohol,  $\kappa_{25^\circ} = 1.45 \times 10^{-6}$ . Even water, however, with an association factor probably between 2 and 3 at ordinary temperatures, has very little conductivity when perfectly pure;  $\kappa_{25^\circ} = 0.55 \times 10^{-7}$ .

It is only when we come to consider fused salts,<sup>10</sup> where the apparent molecular complexity may be as high as 8 to 10, that we find examples of "pure" substances highly dissociated into ions. The following table<sup>11</sup> indicates clearly how specific conductivity varies with association in a

<sup>6</sup> See Kendall and Booge, *loc. cit.*, p. 2327.

<sup>7</sup> The effect of other factors, which will be considered later, must however be borne in mind in the application of this rule. The viscosity of each liquid is a property to be taken into account in any comparison. (See particularly Walden, *Z. physik. Chem.*, **55**, 246 (1906)).

<sup>8</sup> Scudder, "Conductivity and Ionization Constants of Organic Compounds," D. van Nostrand Co., 1914.

<sup>9</sup> Walden, *Z. physik. Chem.*, **46**, 103 (1903). It is probable that the presence of small traces of difficultly removable impurities renders the values given in most cases considerably too high. See Schlesinger and Martin, *THIS JOURNAL*, **36**, 1592 (1914); also the experimental section of the succeeding article.

<sup>10</sup> Walden, *Z. Elektrochem.*, **14**, 723 (1908); Landolt-Börnstein, "Tabellen," 1912, p. 1078.

<sup>11</sup> Compare Turner, *J. Chem. Soc.*, 99, 895 (1911).

typical series of chlorides.<sup>12</sup> Unfortunately a strict comparison at one fixed temperature is impossible.

Substance.	Association Factor. <sup>13</sup>		Specific Conductivity.	
			Mhos.	
NaCl.....	9	(810°)	3.34	(800°)
KCl.....	7	(778°)	2.19	(800°)
AgCl.....	2.25	(451°)	1.83	(500°)
PbCl <sub>2</sub> .....	2.05	(512°)	2.39	(500°)
SbCl <sub>3</sub> .....	1.55	(80°)	1.09	$\times 10^{-4}$ (80°)
POCl <sub>3</sub> .....	1.3	(0°)	2.2	$\times 10^{-6}$ (25°)
AsCl <sub>3</sub> .....	> 1.0	(25°)	1.24	$\times 10^{-6}$ (25°)
HCl.....	> 1.0	(-100°)	2.0	$\times 10^{-7}$ (-100°)
SO <sub>2</sub> Cl <sub>2</sub> .....	1.02	(25°)	1.8	$\times 10^{-7}$ (25°)
CCl <sub>4</sub> ; SiCl <sub>4</sub> .....	1.00	(25°)	about $1 \times 10^{-8}$	(25°)
SnCl <sub>4</sub> ; SbCl <sub>5</sub> .....				
S <sub>2</sub> Cl <sub>2</sub> ; PCl <sub>3</sub>				

Specific conductivity in a pure liquid, therefore, is primarily dependent upon the association factor. To go further we must ask the question: upon what does the degree of association of a pure liquid depend? Examination of the available data shows that here, *just as in two component systems*, the formation of complexes is conditioned primarily by the differences in character (*i. e.*, in the positive or negative nature) of the several groups concerned. Thus in a substance where we have a highly electro-positive and a highly electronegative conjunction, ideal opportunity is afforded for the production of highly associated molecules.<sup>14</sup> When differences in character are less pronounced, less association occurs. We can, indeed, trace a general trend towards increasing or decreasing molecular complexity (so far as our elementary knowledge of association factors allows) as we proceed through any particular series of compounds

<sup>12</sup> The term "*associated*" is hardly adequate to express the condition of fused salts such as NaCl and KCl, the term *polar* being far more pertinent (compare Hildebrand, *THIS JOURNAL*, 38, 1463 (1916)). The fact that the electron has already passed between the atoms has been regarded by most recent investigators, indeed, as establishing that such substances are not associated at all, but completely ionized. The transfer of an electron, however, does not necessitate the independence of the radicals involved, and the use of the term *completely ionized* to include both *free* and *bound* ions is liable to lead to serious confusion of ideas (compare Harkins, *Proc. Nat. Acad. Sci.*, 6, 601 (1920)). Neither *ionized* nor *associated* alone gives a true representation of the state of affairs in a fused salt such as NaCl; the physicist may center his attention upon the passage of the electron and the lack of a definite bond between any two particular ions, while the chemist may lay more stress upon the forces exercised by any one radical upon all oppositely-charged radicals surrounding it and, the consequent "pooling of affinity." The two views are not exclusive but supplementary.

<sup>13</sup> The association factors given are the mean of those obtained by the surface tension method of Ramsay and Shields (*J. Chem. Soc.*, 63, 1099 (1893)) and by the specific cohesion equation of Walden (*Z. physik. Chem.*, 65, 129 (1909)). Other methods of estimating association give here, in several instances, very divergent results (see Walden, *Z. Elektrochem.*, 14, 723 (1908)).

<sup>14</sup> See Kendall and Booge, *loc. cit.*, pp. 2327-8.

arranged in order of the electro-affinity of the variable radical. Thus hydrogen fluoride is highly associated even in the gaseous state and at ordinary temperatures, hydrogen chloride is highly associated only when liquefied, while hydrogen bromide and iodide are only slightly associated even as liquids at low temperatures.<sup>15</sup> In the same way, comparing analogous compounds of succeeding elements in the periodic system, we have "association factors" as follows:  $\text{NaCl} > \text{MgCl}_2 > \text{AlCl}_3 > \text{SiCl}_4$ ; and also,  $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ . Other illustrative examples will readily suggest themselves.<sup>16</sup>

### Ionization in Solutions.

From what has already been said it will be evident that a mixture of two ideal saturated substances (*e. g.*, two hydrocarbons) cannot give a conducting solution, also that the specific conductivity of a solution of an unsaturated substance in a saturated liquid (*e. g.*, hydrogen chloride in a hydrocarbon) will be, in general, exceedingly small.<sup>17</sup>

A mixture of two unsaturated substances, however, affords several possibilities. The results of actual experiment may be separated into three types. In the first, the specific conductivity of the mixture is not widely different from that of its components (usually very small); in the second, the conductivity is markedly greater, but still not exceptionally high; in the third, the conductivity is very great, even if the mixture is formed from two practically non-conducting substances.

The first case is typical of all mixtures in which the two components are similar in character (*i. e.*, for acids and bases, where the acidic or basic strengths are of the same order). Here there will be little or no increase in molecular complexity through compound formation on admixture; the chief effect rather will be mutual dissociation of any complex molecules of the pure components.<sup>18</sup> Hence the conductivity of the solution will not differ greatly from that of its original constituents, and (except in the case of mixtures of fused salts) will always be small. As examples may be cited

<sup>15</sup> See Turner, *J. Chem. Soc.*, 99, 890 (1911).

<sup>16</sup> For full references on this topic see the monograph "Molecular Association," by Turner, (Longmans, Green and Company, 1915).

<sup>17</sup> In any case it will be *less* than that of the unsaturated component when pure, since the degree of association of this component (hence also its tendency towards ionization) will be diminished with the decrease in its concentration.

<sup>18</sup> An apparent exception is the case where both substances are highly associated (*e. g.*, in such a system as phenol: cresol), when compounds of the general type  $(\text{AB})_x$ .  $(\text{CD})_y$  are undoubtedly formed (see Dawson and Mountford, *J. Chem. Soc.*, 113, 923 (1918)). The *average* molecular complexity of such a mixture, however, (and hence its specific conductivity also) will not differ greatly from that of its pure components, since extensive disassociation of these is also involved. The complexes here existent are to be regarded, indeed, not as *substitution* but as *substitution* compounds, as will be shown in detail in a subsequent article.

(a) two very weak electrolytes, water and methyl alcohol;<sup>19</sup> (b) two very strong electrolytes, trichloro-acetic acid in hydrogen bromide.<sup>20</sup> Numerous other instances may be found by reference to Scudder's "Conductivity and Ionization Constants of Organic Substances."

As the characters of the two substances begin to diverge, the extent of compound formation between them will become appreciable. Unless the divergence is very marked, however, the formation of complexes will be limited to the simplest type, and the degree of dissociation of this into its components in the liquid state will be considerable. In other words, the addition of AB to CD involves the production of only a small amount of a new molecular species AB.CD, the least complex (and consequently possessing the least tendency towards ionic disintegration) of all possible compounds. While, therefore, the conductivity of the solution may considerably exceed that of its components, it will still not be especially high. As examples may be given any weak acid or base in water, and hydrogen chloride in formic acid.<sup>21</sup>

If the two substances are decidedly diverse, extensive compound formation will occur on admixture. The complexes formed will include not only the simple type AB.CD but also other and larger molecular species of the general formula  $(AB)_x.(CD)_y$ . Disintegration of these complexes into ions of opposite charge, taking place very readily, will render the solution an exceedingly good conductor. As examples may be given any strong acid or base in water, and methyl alcohol in hydrogen chloride.<sup>22</sup>

The essential features of a solution of high specific conductivity are, therefore: (a) unsaturation in both components; (b) a decided difference in the character of the two components. The first is necessary to enable compound formation to occur at all, the latter is the "driving force" which regulates the increase in molecular complexity (and hence in ionization) on admixture. The following additional examples will illustrate the uniform gradations experimentally observable as these factors are separately varied: (a) *unsaturation*; hydrogen chloride in octane is a non-conductor, in benzene an exceedingly poor conductor, in ether a fair conductor, in alcohol a good conductor, in water an excellent conductor; (b) *diversity*; in liquefied hydrogen chloride<sup>20</sup> as solvent, acetic acid is a good conductor, formic acid not so good, chloro-acetic and cyano-acetic acids poor conductors, trichloro-acetic acid a non-conductor. The conductivity decreases regularly as the acidic strength of the solute approaches that of the solvent. Similarly Walden,<sup>23</sup> considering the

<sup>19</sup> Carrara, *Gazz. chim. ital.*, [I] 27, 422 (1897).

<sup>20</sup> Walker, McIntosh and Archibald, *J. Chem. Soc.*, 85, 1100 (1904).

<sup>21</sup> Zanninovich-Tessarini, *Z. physik. Chem.*, 19, 251 (1896).

<sup>22</sup> Maass and McIntosh, *THIS JOURNAL*, 35, 540 (1913).

<sup>23</sup> Walden, *Trans. Faraday Soc.*, 6, 71 (1910).

conductivity of solutions with water as solute, found that water in liquid hydrogen cyanide is a poor conductor, in formic acid a fair conductor, in sulfuric acid a good conductor.

The examples cited in the foregoing paragraphs furnish valuable cumulative evidence for the presumable validity of the principles underlying the ionization hypothesis here advanced. It must be freely conceded, however, that the greater part of previously recorded work on specific conductivity in non-aqueous solutions has been of a very rough order of accuracy, and it seems scarcely justifiable to base such important generalizations entirely upon isolated measurements of this nature. Consequently, in order to test more systematically the general applicability of the rules regarding ionization outlined above, exact conductivity determinations have been carefully carried out upon several series of typical two-component systems, for each of which the relative extent of compound formation in the liquid state had already been established in earlier articles.

As will be seen by reference to the paper immediately following, the experimental results obtained are in complete accordance with the theory developed, since compound formation and ionization (as given *qualitatively* by specific conductivity)<sup>24</sup> proceed uniformly in parallel throughout each of the systems studied. Where the extent of compound formation is known to be minute, the conductivity is almost immeasurable; as compound formation increases in amount, the conductivity becomes appreciable; where combination is extensive, the conductivity is very markedly increased. A fundamental relationship between the two phenomena is therefore confirmed.

In a later article other factors affecting the formation and stability of addition compounds in solution (such as the influence of ionic volume, of valence, and of temperature) will be discussed. Although these factors are subsidiary to the "diversity factor" here examined, occasional minor divergences from the general rules may be referred to their effect, as will be shown by the consideration of some typical examples.

In conclusion here, it is of importance to indicate how far the above views can be correlated with those expressed by previous investigators in the same field. Owing to the scope of the subject, it is not possible to consider all sides of the question in detail, consequently the discussion will, for space considerations, be limited to two most significant topics—Abegg and Bodländer's theory of complex ions, and Werner's theory of bases and acids. Many other workers have dealt equally intimately and ex-

<sup>24</sup> Specific conductivity is not in itself, of course, an exact measure of the extent of ionization in a solution; other factors (*e. g.*, viscosity, ionic mobility, molecular volume) must also be considered. The corrections introduced by the consideration of these factors will be the subject of a later paper.



tensively with other aspects of the connection between compound formation and ionization in solutions, but reference to their researches must be made directly by the reader.<sup>25</sup>

### The Theory of Complex Ions.

It has been shown in the preceding pages that, in binary solutions, increasing compound formation is regularly accompanied by increasing ionic instability; "union with another molecule promotes ionization." Suppose now that to a binary solution in which there is but little tendency towards ionization we add a third substance which combines very extensively with one of the original components. Obviously the same reasoning will still apply, the increase in molecular complexity will result in increased ionization.

This is Abegg and Bodländer's well-known theory of electro-affinity<sup>26</sup> (which has more recently been restated by Lewis,<sup>27</sup> Hildebrand<sup>28</sup> and Harkins),<sup>29</sup> arrived at from a new angle. Indeed, the whole theory of ionization outlined in this article may be considered, in one sense, as an extension of Abegg and Bodländer's generalizations regarding complex ions to solutions in general.<sup>30</sup> While in a simple substance AB the attractive forces between the constituent radicals usually suffice to inhibit marked ionization, the formation of complexes on addition of a second substance CD will weaken these attractive forces and disintegration of the complex molecules into oppositely charged ions will much more readily occur. Similarly for solutions; a "weak electrolyte" in any given solvent becomes a "stronger electrolyte" by combination with a second solute.<sup>31</sup> As illustrations the following systems may be cited; additional examples are to be found in the article immediately succeeding.

ORIGINAL SYSTEM ("WEAK ELECTROLYTE").	ADDED SUBSTANCE.	RESULTANT COMPOUNDS ("STRONGER ELECTROLYTES").
H <sub>2</sub> O or SO <sub>3</sub>	SO <sub>3</sub> or H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> ; H <sub>2</sub> S <sub>2</sub> O <sub>7</sub> ; H <sub>2</sub> SO <sub>4</sub> ·xH <sub>2</sub> O
NH <sub>3</sub> or H <sub>2</sub> O	H <sub>2</sub> O or NH <sub>3</sub>	NH <sub>4</sub> OH
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O or HCl <sup>32</sup>	HCl or (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O·HCl; (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O·2HCl; (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O·5HCl.

<sup>25</sup> A representative list of references will be found in an earlier article (Kendall and Booge, *THIS JOURNAL*, 39, 2324 (1917)). See also Senter, *Trans. Faraday Soc.*, 15, 4 (1919).

<sup>26</sup> Abegg and Bodländer, *Z. anorg. Chem.*, 20, 453 (1899); 39, 330 (1904).

<sup>27</sup> G. N. Lewis, *THIS JOURNAL*, 38, 762 (1916).

<sup>28</sup> Hildebrand, *ibid.*, 38, 1464 (1916).

<sup>29</sup> Harkins and Hall, *ibid.*, 38, 216 (1916); Harkins and King, *ibid.*, 41, 970 (1919).

<sup>30</sup> The main points of advance are the inclusion of non-aqueous solutions and the insistence upon the equality of solvent and solute in ionization phenomena.

<sup>31</sup> Compare the less definite statement of Lewis (*loc. cit.*): "A slightly polar molecule becomes more strongly polar in the presence of another polar molecular type."

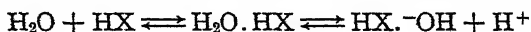
<sup>32</sup> Maass and McIntosh, *THIS JOURNAL*, 35, 538 (1913).

ORIGINAL SYSTEM ("WEAK ELECTROLYTE").	ADDED SUBSTANCE.	RESULTANT COMPOUNDS ("STRONGER ELECTROLYTES").
HCN in H <sub>2</sub> O	Fe(CN) <sub>2</sub>	H <sub>4</sub> Fe(CN) <sub>6</sub>
H <sub>2</sub> CrO <sub>4</sub> in H <sub>2</sub> O	CrO <sub>3</sub>	H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
dimethylpyrone in organic solvents <sup>33</sup>	CCl <sub>3</sub> .COOH	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub> .CCl <sub>3</sub> .COOH; C <sub>7</sub> H <sub>8</sub> O <sub>2</sub> .2CCl <sub>3</sub> .COOH.

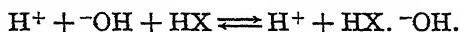
Ionization is thus, essentially, a consequence of compound formation. In certain molecular types, of course, instability may be so extreme that ionic disintegration is appreciable even in the simple molecule (*e. g.*, in the case of liquid iodine;<sup>34</sup>  $I_2 \rightleftharpoons I^+ + I^-$ ). In others, conversely, stability may be so great that ionization is still inappreciable even although the molecule is exceedingly complex (*e. g.*, organic substances in general, although even here the ionic instability of "over-loaded" molecules such as hexaphenylethane<sup>35</sup> may be noted). In solutions in general, however, there is no difficulty in tracing a clear-cut parallelism between increase in molecular complexity and increase in "ionic instability."<sup>36</sup> The analogy of the increasing instability of the atom itself with increasing complexity<sup>37</sup> (*i. e.*, the disintegration of radio-active elements of high atomic weight) is not without interest.

### Werner's Theory of Bases and Acids.

The particular case of aqueous solutions only will be considered here. A fundamental distinction is drawn by Werner between "anhydro-" and "aquo-" bases and acids.<sup>38</sup> "Anhydro-" bases and acids (*e. g.*, NH<sub>4</sub> OH; HCl) are not compounds which dissociate directly, but are compounds from which, *by the addition of water*, the true (or "aquo") bases and acids are produced. Thus, for an acid HX, the following ionization mechanism is postulated,



or



The hydrogen ion in the aqueous solution of such an acid is therefore not produced by the dissociation of the acid, but rather comes directly from the water. Bases and salts are similarly treated, and the conclusion drawn that water plays the chief part in ionization.

<sup>33</sup> Plotnikow, *Ber.*, 39, 1794 (1906); compare Walden, *ibid.*, 34, 4194 (1901); McIntosh, *THIS JOURNAL*, 32, 542 (1910).

<sup>34</sup> Abegg, "Handbuch der anorg. Chem.," [2] 4, 256 (1913).

<sup>35</sup> Gomberg, *THIS JOURNAL*, 36, 1144 (1914).

<sup>36</sup> Thus in all three cases in the table above where more than one complex is formed, the most simple is the most stable; the equimolecular compound exhibits the smallest conductivity.

<sup>37</sup> Subsidiary factors, such as atomic volume, valence, etc., will also induce minor irregularities in this general rule (see p. 1422).

<sup>38</sup> Werner, "New Ideas on Inorganic Chemistry," 1911, pp. 200-219.

While this interpretation is, at first sight, in full accordance with the theory outlined in the present paper, yet on closer examination an important point of difference appears. It is certainly possible to consider water as the *ionizing* substance in all conducting aqueous solutions and to derive thereby a theory of solutions just as satisfactory, in every respect, as that given by the more popular procedure of treating water as merely an inert "medium" for the ionized solute.<sup>39</sup> Either extreme becomes equally illogical, however, as soon as we accept the essential and absolute equality of the two components in a conducting solution.

Ionization in a system  $RX-H_2O$  is, under such a view, regarded as resulting from the disintegration of complexes of the general type  $(RX)_m \cdot (H_2O)_n$ .<sup>40</sup> Cleavage is, of course, *possible* at any point in the complex molecule, and a large number of distinct ionic types may be obtained, the relative concentrations of which will vary with the composition of the solution. There is no *a priori* reason either for the assertion of the ionists that the cleavage necessarily occurs in the  $RX$  molecule, or for Werner's claim that dissociation is restricted to the water molecule. In the great majority of conducting solutions, probably, both species of dissociation take place to extents which cannot be neglected, and consequently the simple equation  $RX \rightleftharpoons R^+ + X^-$  totally fails to reproduce the ionization equilibria. In extreme cases, indeed, such as a "strong electrolyte" in water, the total number of complex molecular and ionic types present must be very large, and since all complex molecules will be, ionically, more unstable than the simple salt, it is evidently quite incorrect to consider the experimental "ionization values" (as ordinarily determined) as representing the actual concentration of the simple ions  $R^+$  and  $X^-$ . Further discussion of this topic must, however, be left for a future communication.

### Summary.

In a preceding article, the formation of solvent-solute complexes has been postulated as a prerequisite to ionization in solutions. Under this assumption, we should be able to predict the degree of dissociation in any given solution from (a) the stability of the complexes with respect to their components, and (b) the instability of the complexes with respect to their ionization products.

The first of these points has been dealt with in detail in previous papers, and the rules formulated have here been extended to the association of

<sup>39</sup> See Kendall and Booge, *THIS JOURNAL*, 39, 2333 (1917).

<sup>40</sup> The structural formula of such complexes and the mechanism of compound formation and ionic disintegration, especially as related to the Lewis-Langmuir theory of valence (Langmuir, *THIS JOURNAL*, 42, 276 (1920)), will be discussed in detail later. For the present, reference should be made to a few preliminary remarks in an earlier article (Kendall and Booge, *ibid.*, 39, 2327 (1917)).

pure liquids. In the present communication the study of the second point—the factors affecting the ionic disintegration of solvent-solute complexes in solution—has been started, and additional generalizations<sup>41</sup> deduced. These generalizations have been shown to be in excellent qualitative agreement with the experimental data of earlier investigators. A more stringent test of their validity has been successfully sought by careful conductivity determinations on specially selected systems, as described in the article immediately succeeding.

The connection between the ionization hypothesis here presented and the views of Abegg and Bodländer on the one hand, and of Werner on the other, has been briefly examined and some points of difference indicated.

In a future article the factors affecting the formation and stability of addition compounds in solution will be further discussed, and the problem of strong electrolytes investigated.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY,  
No. 362.]

## COMPOUND FORMATION AND SPECIFIC CONDUCTIVITY IN SOLUTIONS OF THE TYPES ACID:ESTER, ACID:KETONE AND ACID:ACID.

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Received January 11, 1921.

As explained in the preceding article,<sup>1</sup> the purpose of this investigation is to test, more stringently than can be done by existent data, the general validity of the hypothesis that ionization in solutions is dependent upon preliminary compound formation between solvent and solute. Careful conductivity determinations through the whole concentration range (pure solvent to pure solute) have here been carried out upon several series of typical two-component systems, for the different members of which the relative extent of compound formation in the liquid state has already been established<sup>2</sup> by a study of their freezing-point curves.

For the first series, systems of the general type  $HX:R.COOR'$  were chosen. It has been shown previously<sup>2</sup> that, in such systems, the extent of compound formation increases regularly as the radicals R and R' of the ester are made more electropositive, or as the radical X of the acid is made more electronegative. A suitable variation of all 3 radicals has been ensured in this work by selecting the following systems for examination:

<sup>41</sup> See pp. 1420–22.

<sup>1</sup> Kendall and Gross, *THIS JOURNAL*, **43**, 1416 (1921).

<sup>2</sup> Kendall and Booge, *ibid.*, **38**, 1712 (1916).

acetic acid (a typical weak acid) and trichloro-acetic acid (a typical strong acid) with each of the 3 esters, ethyl acetate, ethyl benzoate and benzyl benzoate.

For the second series, systems of the general type,  $HX:R.CO.R'$  were taken. Freezing-point data for such systems show<sup>3</sup> that here also the extent of compound formation increases as the radicals  $R$  and  $R'$  of the ketone are made more electropositive, or as the radical  $X$  of the acid is made more electronegative. The following representative systems were studied: acetic acid and trichloro-acetic acid with acetone and acetophenone.

For the third series, systems of the general type,  $HX:HY$  were selected. Compound formation between acids in pairs has been shown<sup>4</sup> to increase regularly with increasing diversity in the electro-affinity of the radicals  $X$  and  $Y$ . In this work acetic acid was taken as the fixed component  $HX$ , and acids of widely divergent character (trichloro-acetic, a typical strong acid; monochloro-acetic, a typical transition acid; and propionic, a typical weak acid similar to acetic) chosen as the variable component  $HY$ . A considerable range in compound formation through the series was thus obtained. This series was also still further extended<sup>5</sup> by including some examples of the type, acid: base, for which reliable data are already available.<sup>5</sup> An additional system of this class, acetic acid: formamide, was here investigated for comparison.

### Experimental.

**Purification of Materials.**—The nature of the experimental work rendered it necessary to take extreme precautions to ensure the elimination of even minute traces of impurities from all substances employed. The presence of impurities in quantities insufficient to exert any appreciable influence upon the freezing point or boiling point was frequently found to result in a very considerable change in specific conductivity.<sup>6</sup> A constant specific conductivity was therefore made the final criterion of purity. After other satisfactory physical constants had been obtained, purification was continued until no further lowering in the specific conductivity could be effected. Brief descriptions of the methods of purification adopted will be found under the separate systems below. Here the measure of success attained may be indicated by comparing the results of this work with the lowest values previously recorded. The association factors<sup>7</sup> and viscosities<sup>8</sup> for each liquid are included for convenience of reference in subsequent discussion.

<sup>3</sup> Kendall and Gibbons, *THIS JOURNAL*, 37, 149 (1915).

<sup>4</sup> Kendall, *ibid.*, 36, 1722 (1914).

<sup>5</sup> Patten, *J. Phys. Chem.*, 6, 580 (1902).

<sup>6</sup> See also Walden, *Z. physik. Chem.*, 46, 121 (1903); Schlesinger and Martin, *THIS JOURNAL*, 36, 1592 (1914); Davis, Putnam and Jones, *J. Franklin Inst.*, 180, 577 (1915).

<sup>7</sup> Walden, *Z. physik. Chem.*, 39, 561 (1902).

<sup>8</sup> Kendall and Wright, *THIS JOURNAL*, 42, 1776 (1920); unpublished data by Kendall and Brakeley; Merry and Turner, *J. Chem. Soc.*, 105, 758 (1914).

TABLE I.—SPECIFIC CONDUCTIVITIES OF PURE LIQUIDS.

Liquid.	Association factor.	$\eta$ 25°.	$\kappa$ 25° (Kendall and Gross).	$\kappa$ 25° (previous record).
Ethyl acetate <sup>9</sup> .....	1.00	0.004239	$<1 \times 10^{-9}$	$4 \times 10^{-7}$
Ethyl benzoate.....	1.00	0.02014	$<1 \times 10^{-9}$	.....
Benzyl benzoate.....	1.00	0.08514	$<1 \times 10^{-9}$	.....
Acetone <sup>10</sup> .....	1.26	0.003065	$5.8 \times 10^{-8}$	$15 \times 10^{-8}$
Acetophenone <sup>11</sup> .....	1.16	0.01681	$5.5 \times 10^{-8}$	$18 \times 10^{-8}$
Acetic acid <sup>12</sup> .....	3.62	0.01121	$2.4 \times 10^{-8}$	$2 \times 10^{-8}$
Propionic acid <sup>13</sup> .....	$>1.0$	0.0102	$<1 \times 10^{-9}$	$7 \times 10^{-8}$
Monochloro-acetic acid. $>1.0$	.....	.....	$1.4 \times 10^{-6}$ (60°)	.....
Trichloro-acetic acid <sup>14</sup> . $>1.0$	.....	0.0397 (60°)	$6.2 \times 10^{-9}$ (60°)	$1 \times 10^{-7}$ (60°)
Formamide <sup>15</sup> .....	6.18	0.03358	$4 \times 10^{-6}$	$3 \times 10^{-6}$

**Temperature Regulation.**—Wherever practicable, determinations were carried out at 25°, in a large Freas thermostat electrically regulated to  $\pm 0.01^\circ$ . In the case of solutions containing considerable excess of trichloro-acetic or monochloro-acetic acid, it was not possible to obtain direct measurements at 25°, since the systems start to solidify above that temperature, and supercooling to any large extent in the presence of the platinum electrodes could not be successfully maintained. The curves for systems containing these acids as one component were consequently completed by carrying out determinations, where necessary, at a higher temperature (60°) and transposing the results so obtained to values approximately correct for 25° by the use of a temperature coefficient derived from the last solution measurable at the lower temperature. The assumption that the temperature coefficient is independent of concentration renders, of course, such transposed values rather uncertain, but as will be seen by reference to the diagrams<sup>16</sup> the portions of the curves so treated are of only minor importance, and the results obtained are sufficiently accurate to indicate the essential course of the completed curves. The determinations at 60° were carried out in a smaller thermostat, fitted with an Ostwald regulator and showing variations in temperature of less than  $\pm 0.05^\circ$ .

**Conductivity Measurements.**—The specific conductivities of the solutions examined varied from  $6 \times 10^{-8}$  to less than  $1 \times 10^{-9}$  mhos, the latter value constituting the lower limit of the measurable range with the apparatus employed. In order to obtain good sound minima with the more poorly conducting solutions, cells of the

<sup>9</sup> Kahlenberg and Lincoln, *J. Phys. Chem.*, 3, 12 (1899). Sammis (*ibid.*, 10, 593 (1906)) states that ethyl acetate shows zero conductivity, but does not indicate his limits of measurement.

<sup>10</sup> Walden, *Z. physik. Chem.*, 73, 263 (1910).

<sup>11</sup> Lincoln, *Trans. Wisconsin Acad.*, 12, II, 395 (1898-9).

<sup>12</sup> Patten, *J. Phys. Chem.*, 6, 654 (1902). It must be noted that Patten worked with cells possessing much larger constants than those here employed, and also used a short bridge. His value for  $\kappa$  can consequently be only an approximation, since it is right at the lower limit of measurable conductivities.

<sup>13</sup> Otten, *Diss.*, München, 1887.

<sup>14</sup> Whetham, *Phil. Mag.*, [5] 44, 1 (1897). The material employed was evidently very impure, since its m. p. (52°) was more than 7° below that of the acid used in this work.

<sup>15</sup> Davis and Putnam, *J. Franklin Inst.*, 180, 577 (1915). Only a very small fraction of material with  $\kappa = 3 \times 10^{-6}$  was obtained by these investigators, the formamide actually employed in their conductivity measurements having much higher values,  $\kappa = 7 \times 10^{-6}$  to  $15 \times 10^{-6}$ .

<sup>16</sup> Dotted curves, in the diagrams, indicate values reduced from 60°.

special type described by Beans and Eastlack<sup>17</sup> were used throughout. The electrodes were carefully platinized and the cell constants (which ranged, for different cells, between 0.007 and 0.009) were frequently redetermined during the course of the determinations. As noted by Beans and Eastlack, the passage of the current caused no appreciable heating effects with the solutions investigated. Capacity errors were tested for, and found to be within the errors of measurement.

The bridge employed was a 3-meter Leeds and Northrup instrument; the accuracy of the bridge calibrations and of the attached resistances was thoroughly checked throughout the work. Alternating current at 1000 cycles per second was obtained from a constant-speed high-frequency generator. The telephone receiver used was tuned to the same frequency.

Conductivity measurements were made, for each system, at a sufficient number of different concentrations to define the complete curve, the distance between successive points being varied to suit each particular case. Mixtures were made up by direct weighing, with the use of a Grethan pipet for the liquids. The molecular composition values tabulated below are accurate within  $\pm 0.05\%$ . The accuracy of the conductivity data does not approach this in order. For poorly conducting solutions ( $\kappa < 10^{-7}$ ) the error limit is from 1 to  $2 \times 10^{-9}$ . For solutions of higher conductivity, the values given are accurate to 0.5 or 1.0% for systems of the types acid: ester and acid:acid, and from 1.0 to 2.0 % for systems of the types acid: ketone and acid:base. The main source of error lies in the difficulty of preparing materials of constant purity. In particular cases (*i.e.*, in systems containing acetone or formamide) the limits of error may even exceed 2.0%, owing to the impossibility of keeping an adequately purified product entirely unchanged during the determinations. The problem here presents the same difficulties as does the preparation of ultra-conductivity water.<sup>18</sup>

Even the largest possible error which may thus be introduced, however, is negligible when the relative positions of the conductivity curves for different systems are compared, as will be seen below.

### Systems of the Type, Acid: Ester.

**Trichloro-acetic Acid: Ethyl Acetate.**—Trichloro-acetic acid (reputed c. p.) was dissolved in hot benzene and precipitated as fine crystals by rapid cooling. The crystals were repeatedly washed with cold benzene and the washings drained off. The residual crystals, with adherent benzene, were then liquefied by heating and the hot solution poured into a crystallizing dish over 99% sulfuric acid in a vacuum desiccator. Crystals of trichloro-acetic acid were deposited on cooling, and the last traces of benzene were completely removed by absorption and sulfonation in the sulfuric acid. The melting point of the product thus obtained,  $59.4^\circ$ , is the highest yet recorded.<sup>19</sup>

<sup>17</sup> Beans and Eastlack, *THIS JOURNAL*, 37, 2674 (1915).

<sup>18</sup> See Kendall, *ibid.*, 38, 2460 (1916).

<sup>19</sup> See Kendall and Booge, *ibid.*, 38, 1723 (1916). Owing to the extremely tremely hygroscopic character of trichloro-acetic acid, work on systems in which it formed one component was restricted to dry, cold days. Considerable patience was occasionally necessary.

Ethyl acetate was purified by careful fractionation, according to the recommendations of Wade.<sup>20</sup> The sample employed gave a boiling point of  $77.1 \pm 0.05^\circ$ .

The specific-conductivity data for the complete system are given below. Compositions of mixtures are expressed in molecular percentages; conductivities are given in reciprocal ohms  $\times 10^7$ ; the temperature is  $25^\circ$  unless otherwise noted. The results are also reproduced graphically in Fig. 1.

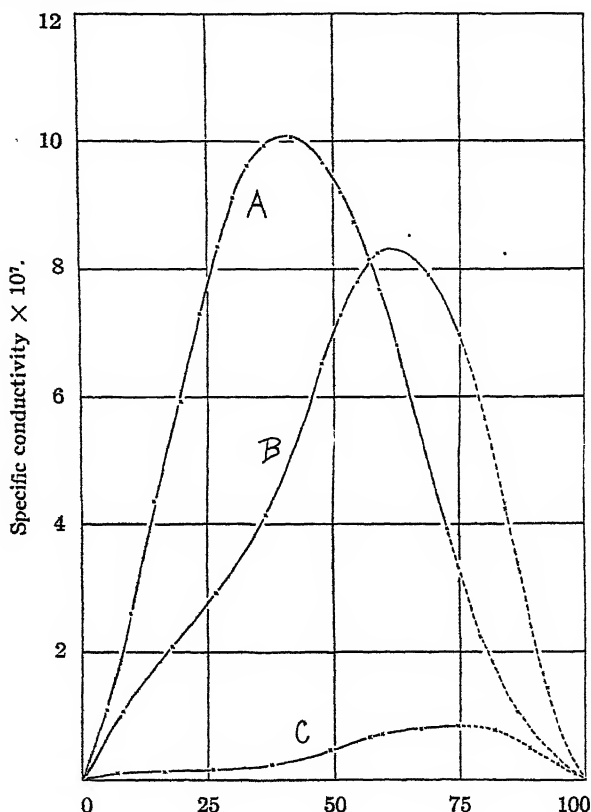


Fig. 1.—Systems of the type acid:ester. Curve A, trichloro-acetic acid:ethyl acetate; Curve B, trichloro-acetic acid:ethyl benzoate; Curve C, trichloroacetic acid:benzyl benzoate.

Mol % acid	0.0	4.93	9.80	14.86	19.55	23.56	27.31	30.07
$\kappa \times 10^7$	<0.01	1.10	2.59	4.36	5.94	7.32	8.37	9.12
Mol % acid	33.06	36.67	42.05	48.05	51.52	54.34	57.22	59.07
$\kappa \times 10^7$	9.62	9.95	10.05	9.67	9.19	8.74	8.11	7.68
Mol % acid	63.16	72.63	72.63	79.12	86.40	...		
$\kappa \times 10^7$	6.82	3.93	7.02(60°)	44.01 (60°)	1.91(60°)			
Mol % acid	94.66		100.0					
$\kappa \times 10^7$	0.37 (60°)		0.06(60°)					

<sup>20</sup> Wade, *J. Chem. Soc.*, 87, 1656 (1905).



**Acetic Acid:Ethyl Acetate.**—Acetic acid was first partially purified by successive fractional crystallizations of c. p. glacial acid. It is an exceedingly laborious and wasteful process to remove all traces of water by this method,<sup>21</sup> consequently the following alternative procedure was devised. The freezing-point of a partially purified product was carefully determined and the water content calculated from the amount of divergence from the standard value, using the figures of De Visser.<sup>22</sup> The exact quantity of redistilled acetic anhydride necessary for the conversion of this water to acetic acid was then added and complete hydrolysis effected by refluxing the liquid at the boiling point for 30 hours, taking care to exclude moisture.<sup>23</sup> The acid so obtained was carefully fractionated and the main fraction (b. p.,  $117.8^\circ \pm 0.1^\circ$ ; m. p.,  $16.57^\circ \pm 0.05^\circ$ ) employed in the conductivity work. The results are given below and in Fig. 1.

Mol % acid.....	0.00	23.52	49.27	77.87	100.0
$\kappa \times 10^7$ .....	<0.01	0.05	0.12	0.20	0.24

**Trichloro-acetic Acid: Ethyl Benzoate.**—Ethyl benzoate, reputed c. p., was fractionated repeatedly under ordinary pressure. The fraction with constant boiling point  $212.9^\circ \pm 0.1^\circ$  was employed.<sup>24</sup>

Mol % acid	0.00	7.95	17.93	26.83	36.59	47.66	51.37	54.81
$\kappa \times 10^7$	<0.01	1.19	2.08	2.91	4.14	6.32	7.28	7.80
Mol % acid	58.88	68.72	68.72	74.97	84.32	92.57	100.0	
$\kappa \times 10^7$	8.26	7.91	13.91	12.24	7.57	2.54	0.06	
			(60°)	(60°)	(60°)	(60°)	(60°)	

**Acetic Acid:Ethyl Benzoate.**—

Mol % acid.....	0.00	10.15	28.78	44.07	61.45	74.69	84.60	91.74	100.0
$\kappa \times 10^7$ .....	<0.01	0.04	0.08	0.16	0.28	0.38	0.43	0.38	0.24

**Trichloro-acetic Acid:Benzyl Benzoate.**—Attempts to purify benzyl benzoate by distillation under ordinary pressure, as recommended by the Earl of Berkeley,<sup>25</sup> gave a product of inconstant specific conductivity, probably due to slight cracking at the high temperature required (corrected b. p.,  $323.0^\circ \pm 0.2^\circ$ ). An improved form of apparatus<sup>26</sup> for fractionation under constant low pressure (about 20 mm.) was devised, and a satisfactory product obtained by repeating the distillation of the best fraction until no further change in its physical constants could be effected.<sup>27</sup>

<sup>21</sup> See Bousfield and Lowry, *J. Chem. Soc.*, 99, 1432 (1911); DeVisser, *Rec. trav. chim. Belg.*, 12, 101 (1893). Ballo (*Z. physik. Chem.*, 72, 439 (1910)) claims that acetic acid and water form solid solutions.

<sup>22</sup> De Visser, *loc. cit.*, p. 118.

<sup>23</sup> Johnstone (*Trans. Nova Scotia Inst. Science*, 13, 199 (1913-14)) attempted this method, but found the specific conductivity of his product higher than at first. This he attributed to traces of HCl in the anhydride employed; more probably, however, it was due to incomplete hydrolysis.

<sup>24</sup> Timmermans, *Bull. soc. chim. Belg.*, 25, 316 (1911).

<sup>25</sup> Earl of Berkeley, *J. Chem. Soc.*, 109, 520 (1916).

<sup>26</sup> See Gross and Wright, *J. Ind. Eng. Chem.*, 13, 701 (1921).

<sup>27</sup> The m. p. of the final product was  $19.3^\circ \pm 0.05^\circ$ . Values as high as  $21^\circ$  are to be found in the literature (see Claisen, *Ber.*, 20, 647 (1887)), but such values, being based without exception upon measurements made by the capillary-tube method upon small amounts of material with unstandardized thermometers, are worthless for comparison. More recent work establishes  $19.4^\circ \pm 0.05^\circ$  as the most probable m. p. for a perfectly pure product (see Kendall and Monroe, *This Journal*, 43, 115 (1921)).

Mol % acid	0.00	6.94	16.25	26.05	37.58	49.28	57.01	59.54	67.25
$\kappa \times 10^7$	<0.01	0.12	0.13	0.16	0.23	0.47	0.68	0.73	0.80
Mol % acid	74.72	74.72	81.96		88.96		94.50		100.00
$\kappa \times 10^7$	0.84	2.28 (60°)	2.17 (60°)		1.37 (60°)		0.70 (60°)		0.06 (60°)

## Acetic acid : Benzyl Benzoate.—

Mol % acid.....		0.00	22.76	73.81	100.0
$\kappa \times 10^7$ .....		<0.01	< 0.01	< 0.01	0.24

## Systems of the Type, Acid : Ketone.

Trichloro-acetic Acid : Acetone.—The difficulties encountered in the purification of acetone have been noted by many previous investigators.<sup>28</sup> Impurities other than water can be removed by forming and separating the bisulfite addition compound, hydrolyzing, and fractionating repeatedly. The real task, however, still remains—the total elimination of water. The method proposed by Shipsey and Warner<sup>29</sup> was attempted, but the resulting product (although satisfactory in its other physical constants) possessed too high a specific conductivity for use in this work. The procedure finally resorted to was that recommended by Timmermans<sup>30</sup>—dehydration by means of phosphorus pentoxide. Acetone of low conductivity was thus obtained and carefully fractionated. In spite of all precautions, however, it was found that the conductivity of the purest material prepared could not be kept constant, but increased slowly on standing.<sup>31</sup> Freshly fractionated acetone was consequently always employed in the preparation of the solutions listed below, and conductivity measurements carried out as rapidly as possible, consistent with accurate work. Even so, great difficulty was experienced in duplicating some of the individual points in trichloro-acetic acid—acetone mixtures, the deviations between different preparations amounting in some cases to 5%. The uncertainty thus introduced in the conductivity data, however, does not affect their relative magnitude as compared with the values for other systems, as may be seen most readily by reference to Fig. 2.

Mol % acid	0.00	3.37	6.76	10.05	12.52	16.28	19.53	23.04	26.02
$\kappa \times 10^7$	0.58	88.6	128.4	163.0	198.5	214.5	222.9	224.8	218.9
Mol % acid	28.57	31.81	40.04	47.32	54.17	59.74	65.79	72.47	
$\kappa \times 10^7$	205.1	183.4	144.1	118.0	95.7	73.8	54.4	33.1	
Mol % acid	76.60		76.60		92.66		100.0		
$\kappa \times 10^7$	20.23		36.01 (60°)		2.57 (60°)		0.06 (60°)		

## Acetic Acid : Acetone.—

Mol % acid.....	0.00	12.56	20.27	28.65	39.45	46.03	51.04	64.92	
$\kappa \times 10^7$ .....		0.58	3.02	3.46	4.19	4.42	4.58	5.08	4.80
Mol % acid.....		71.43	81.10	92.23	100.0				
$\kappa \times 10^7$ .....		4.32	3.12	1.33	0.24				

<sup>28</sup> See, for example, Walden, *Z. physik. Chem.*, **46**, 124 (1903); Timmermans, *Bull. soc. chim. Belg.*, **24**, 244 (1910).

<sup>29</sup> Shipsey and Warner, *J. Chem. Soc.*, 103, 1255 (1913).

<sup>30</sup> Timmermans, Reference 28. A considerable loss of material results from the action of the pentoxide on the acetone itself.

<sup>31</sup> This increase may be accounted for either by the absorption of minute amounts of impurities which affect the conductivity tremendously (as CO<sub>2</sub> from the air does in the case of water) or by the steady progress of isomeric (keto-enol) or polymeric changes on standing.

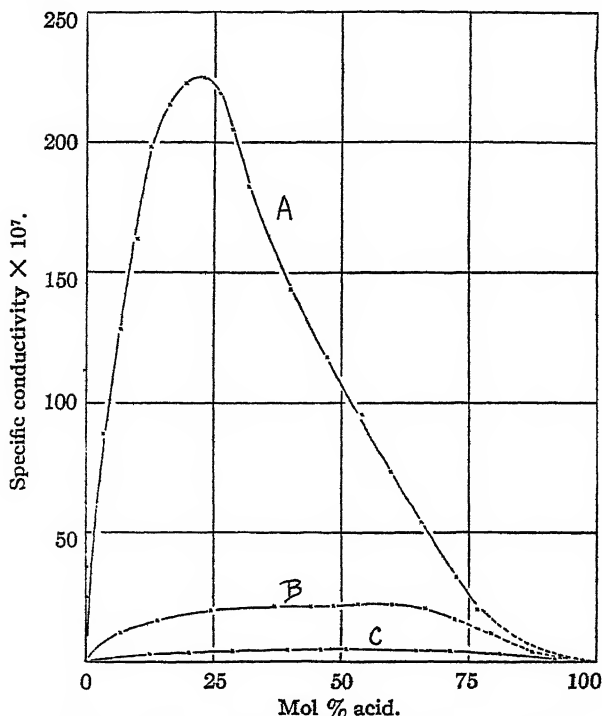


Fig. 2.—Systems of the type acid ketone. Curve A, trichloro-acetic acid:acetone; Curve B, trichloro-acetic acid:acetophenone; Curve C, acetic acid:acetone.

**Trichloro-acetic Acid:Acetophenone.**—Acetophenone (reputed c.p.) was dehydrated with phosphorus pentoxide and repeatedly fractionated<sup>32</sup> under ordinary pressure. The material finally employed was of constant boiling point ( $202.3^\circ \pm 0.1^\circ$ ), with specific conductivity<sup>33</sup>  $5.5 \times 10^{-8}$ .

The results given below are also reproduced graphically in Fig. 2.

Mol % acid	0.00	6.83	14.04	24.60	36.92	44.15	48.42	53.23
$\kappa \times 10^7$	0.55	11.39	15.96	20.10	21.35	21.41	21.66	22.38
Mol % acid	59.94	66.64	71.37	72.42	71.37	79.27	87.38	
$\kappa \times 10^7$	22.57	20.84	17.77	16.88	44.43	(60°) 27.94	(60°) 10.57	(60°)
Mol % acid	95.16	100.0						
$\kappa \times 10^7$	1.48	(60°)	0.06	(60°)				

**Acetic Acid:Acetophenone.**—

Mol % acid	0.00	6.91	16.39	25.39	33.29	40.98	49.55	57.22
$\kappa \times 10^7$	0.55	2.86	3.33	3.51	3.58	3.46	3.44	3.20
Mol % acid	65.87	69.68	77.20	82.79	90.74	100.0		
$\kappa \times 10^7$	2.83	2.59	2.26	1.75	1.11	0.24		

<sup>32</sup> The acetophenone was carefully decanted off from the pentoxide before distilling so as to avoid the possible formation of benzoic acid during fractionation. Compare Klago and Allendorf, *Ber.*, 31, 1298 (1898).

<sup>33</sup> The value given here could probably be still further reduced, since very small fractions with somewhat lower conductivities were obtained.

## Systems of the Type, Acid:Acid.

**Trichloro-acetic Acid:Acetic Acid.**—The results for this system are shown in graphic form in Fig. 3.

Mol % trichloro-acetic acid	0.00	4.86	10.43	18.72	23.72	27.67	31.75	37.99
$\kappa \times 10^7$	0.24	1.67	3.67	6.37	8.05	8.31	8.08	7.10
Mol % trichloro-acetic acid	44.87	52.39	60.39	68.34	71.73	71.73,		
$\kappa \times 10^7$	5.64	3.80	2.25	1.15	0.84	2.91 (60°)		
Mol % trichloro-acetic acid		82.37		90.53		100.0		
$\kappa \times 10^7$		1.04 (60°)		0.38 (60°)		0.06 (60°)		

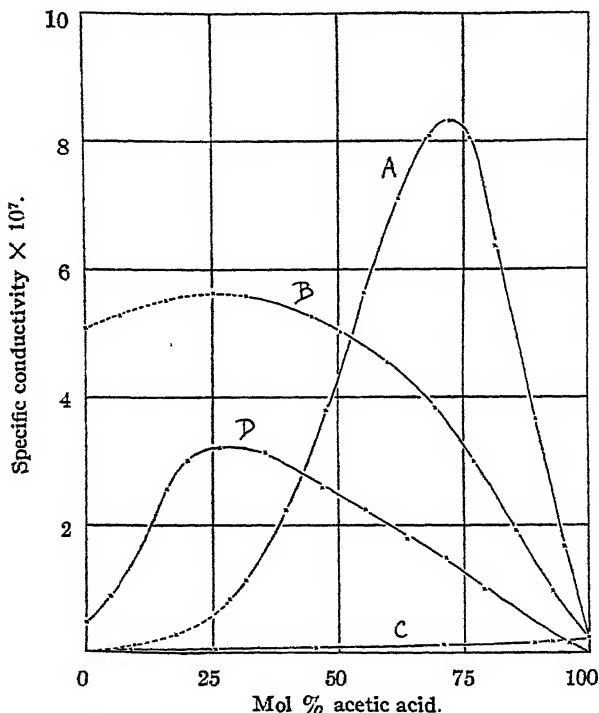


Fig. 3.—Systems of the type acid: acid. Curve A, trichloro-acetic acid:acetic acid; Curve B, monochloro-acetic acid:acetic acid; Curve C, propionic acid:acetic acid; Curve D, formamide:acetic acid(reduced to 1/200).

**Monochloro-acetic Acid:Acetic Acid.**—Monochloro-acetic acid was recrystallized from benzene and fractionated under atmospheric pressure. A large constant-boiling fraction was obtained, which was again crystallized several times from benzene, as described under trichloro-acetic acid.<sup>34</sup> The final product possessed an exceptionally high specific conductivity<sup>35</sup> for a pure substance,  $\kappa_{60^\circ} = 1.4 \times 10^{-6}$ . Further

<sup>34</sup> See p. 1429.

<sup>35</sup> No previous values are recorded in the literature. It is of interest to note, however, that the dielectric constant is also exceptionally high (Walden, *Z. physik. Chem.* 70, 569 (1909)).

attempts at purification, however, did not result in any reduction. The specific conductivity curve for the system is shown in Fig. 3.

Mol % monochloro-acetic acid	0.00	7.25	14.76	23.02	30.50	40.16	49.60	55.20
$\kappa \times 10^7$	0.24	0.98	1.92	2.99	3.84	4.55	5.03	5.27
Mol % monochloro-acetic acid	68.21	68.21	74.81	84.13	93.20	100.0		
$\kappa \times 10^7$	5.59	15.54	15.64	15.33	14.67	14.1		
	(60°)	(60°)	(60°)	(60°)	(60°)	(60°)		

**Propionic Acid : Acetic Acid.**—Propionic acid, with no measurable conductivity, was prepared from a reputed C. P. product by fractional distillation. The results are reproduced in Fig. 3.

Mol % propionic acid.....	0.00	7.51	28.80	54.59	74.63	91.14	100.0
$\kappa \times 10^7$ .....	0.24	0.18	0.13	0.07	0.06	0.03	<0.01

**Formamide : Acetic Acid.**—The formamide employed had been prepared by heating ammonium formate. The removal of traces of decomposition products formed during this preparation was found to be a matter of extreme difficulty. Partial crystallization did not prove successful,<sup>36</sup> but a product of sufficient purity was finally secured by careful fractionation *in vacuo*. The specific conductivity of the best fraction obtained was  $4 \times 10^{-6}$ . The amount of this fraction was too small for making up a complete series of solutions, and the values given below were derived with the use of material of a higher conductivity;  $\kappa = 9 \times 10^{-6}$ . Previous investigators<sup>37</sup> have encountered similar difficulties in the preparation of a standard product and have adopted the same procedure. While the results thus obtained are naturally not so reliable as in the case of other systems, yet for purposes of comparison their degree of accuracy is amply sufficient (see Fig. 3).

Mol % formamide.....	0.00	4.00	11.08	21.05	28.42	36.42	44.74	53.15
$\kappa \times 10^7$ .....	0.24	4.36	33.88	201.4	300.5	380.3	448.1	515.7
Mol % formamide.....	64.48	73.41	80.01	84.11	95.18	100.0		
$\kappa \times 10^7$ .....	629.2	641.8	605.4	515.0	177.2	91.4		

### Consideration of Results.

**Pure Liquids.**—The connection between association and self-ionization in pure liquids, discussed in the preceding article, is typically illustrated by the data presented in Table I. The esters, which are practically non-associated, also exhibit practically zero conductivity. The ketones and acids, with higher degrees of association, possess specific conductivities in general of a higher order. In view of the uncertainty in some of the values,<sup>38</sup> this qualitative agreement with theory is all that can be demonstrated here. For strict comparison purposes, moreover, differences in viscosity and ionic mobilities in the various liquids must also be taken into account.

<sup>36</sup> Braun, *THIS JOURNAL*, **40**, 793 (1918).

<sup>37</sup> Davis and Putnam, *J. Franklin Inst.*, **180**, 577 (1915). These investigators find that solutions with formamide as one component show little difference in specific conductivity, whether material of  $\kappa = 7 \times 10^{-6}$  or  $\kappa = 15 \times 10^{-6}$  is employed.

<sup>38</sup> Some of the figures given (*e. g.*, for formamide) are certainly too high. In most cases, however, it is doubtful whether further attempts at purification would lower the specific conductivity appreciably. Such drastic changes in the accepted values as have here been effected are, at any rate, not likely to recur.

**Solutions.**—The conductivities of the mixtures investigated are, except in such cases where the "diversity factor" is negligible,<sup>39</sup> considerably in excess of those of the pure components, as will be evident by inspection of the diagrams. The maxima on the curves are listed below. Where compounds have been isolated by the examination of the freezing-point curve of the system, their formulas and melting points are also indicated. In order to economize space in presenting formulas, the letters A and B are used throughout to indicate the first and second components of each system.

TABLE II.—MAXIMUM SPECIFIC CONDUCTIVITIES OF MIXTURES.

System.	Max. spec. cond. (mhos.X10 <sup>7</sup> ).	Composition of solution of max. cond. (Mol. % component A).	Compounds isolated.	M. p. (° C.).
Trichloro-acetic acid: ethyl acetate.....	10.1	41	AB	—27
Trichloro-acetic acid: ethyl benzoate...	8.3	61	AB	—23
Trichloro-acetic acid: benzyl benzoate..	0.84	75	AB	+11.9
Acetic acid: ethyl benzoate.....	0.44	83	..	..
Trichloro-acetic acid: acetone .....	225.0	22	..	..
Trichloro-acetic acid: acetophenone ....	22.6	58	AB	+26
Acetic acid: acetone .....	5.1	53	..	..
Acetic acid: acetophenone.....	3.6	33	..	..
Trichloro-acetic acid: acetic acid.....	8.3	28	..	..
Monochloro-acetic acid: acetic acid.....	5.6	75	..	..
Formamide: acetic acid.....	646.0	72	AB <sub>2</sub>	40 —8

In no case does the position of the maximum point correspond with the composition of the isolable compound, or indeed, except by chance, with any simple molecular proportions of the two components. No exact correspondence, however, although frequently sought for by earlier investigators,<sup>41</sup> is to be expected, even under the assumption here made that the conductivity of the mixtures is to be ascribed to the ionic instability of the addition compounds formed. For, in the first place (as may be seen from Table I), considerable changes in viscosity occur in any given system as composition is varied, and such viscosity changes will necessarily be accompanied by variations in the mobilities of the ions. The point of highest ionic concentration is not, in consequence, the point of highest specific conductivity.<sup>42</sup> A second disturbing factor of equal importance is the change in average ionic complexity with change in composition. Addition compounds other than the equimolecular are certainly present in solutions of the types here studied,<sup>43</sup> even although their concentration

<sup>39</sup> E. g., in the systems, acetic acid: propionic acid; acetic acid: ethyl acetate.

<sup>40</sup> English and Turner, *J. Chem. Soc.*, 107, 777 (1915).

<sup>41</sup> For references see Carrara, *Ahrens' Sammlung*, 12, 403 (1908); Dhar, *Z. Elektrochem.*, 20, 57 (1914).

<sup>42</sup> The viscosity curves of the systems here examined will be presented in a subsequent paper.

<sup>43</sup> See Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2305 (1917).

may not be sufficient to permit of their actual isolation. The relative amounts of the various compounds will vary with the solution, each compound (according to the law of mass action) being present in maximum quantity in a solution of its own composition. Each compound, furthermore, will have its own particular "ionic instability," the most simple in type, the equimolecular, being also the least unstable. We can hardly postulate, therefore, a *maximum* specific conductivity for the solution of equimolecular composition when compounds of more complex character, although present in smaller amounts, may exhibit very superior tendencies towards ionic disintegration. In certain cases, indeed, where the equimolecular compound is exceptionally stable and where other compounds, much less stable in comparison, are also formed in quantity, we may expect to find not a maximum but a *minimum* specific conductivity for the equimolecular solution. Actual examples of this type are discussed later.

How far the predicted parallelism between compound formation and ionization is experimentally realized in the systems examined may now be briefly discussed.

**Systems of the Type Acid:Ester.**—According to the rules outlined in the introduction, solutions of trichloro-acetic acid with ethyl acetate should show the highest conductivities of all those here studied, followed by solutions of the same acid with ethyl benzoate and benzyl benzoate. The three esters with acetic acid should exhibit very much lower conductivities.

Inspection of Fig. 1 and Table II will show that this is the case. At the one extreme we have the system trichloro-acetic acid:ethyl acetate, with a maximum specific conductivity of  $10 \times 10^{-7}$ , at the other extreme the system acetic acid:benzyl benzoate, with conductivities immeasurably small. The only break in the regularity consists in the slight superiority of the system acetic acid:ethyl benzoate over the system acetic acid:ethyl acetate. The conductivities throughout both of these systems, however, are only of the same order as that of pure acetic acid.

**Systems of the Type Acid:Ketone.**—Employing our theory as before, we may predict here that solutions of trichloro-acetic acid with acetone will possess higher conductivities than those of the same acid with acetophenone, and that the two ketones with acetic acid will give much more poorly conducting solutions. Again the experimental results are in agreement, as may be seen from Fig. 2 and Table II.

The conductivities in this series are very much greater than in corresponding ester systems; for example, the system trichloro-acetic acid:acetone shows a maximum specific conductivity of  $225 \times 10^{-7}$ . This must be ascribed to the "unsaturation factor," discussed in the preceding article,<sup>44</sup> the ketones being typical associated liquids while the esters are practically non-associated.

<sup>44</sup> P. 1421.

**Systems of the Type Acid : Acid.**—While very high conductivities are not to be expected here, yet the large range in the "diversity factor" through the series should be reflected in correspondingly large variations in the specific conductivities obtained. In actual fact, we find the system of two very dissimilar acids trichloro-acetic acid:acetic acid with a maximum value of  $8.3 \times 10^{-7}$ , while the system of two essentially similar acids propionic acid:acetic acid possesses negligible conductivities throughout. The curve for the system monochloro-acetic acid:acetic acid is intermediate in its position.

**Systems of the Type Acid : Base.**—The increase in the "diversity factor" here results in vastly increased compound formation and specific conductivity in the solutions. Thus even an exceedingly weak base such as formamide gives an isolable addition product with acetic acid, and the maximum specific conductivity exceeds  $600 \times 10^{-7}$ . Water, another very weak base, gives a much more pronounced maximum.<sup>45</sup> Solutions of stronger bases, such as the substituted alkyl and aryl amines, give still higher conductivities with acetic acid. Our uncertainty as to the actual strengths of such bases renders close comparison difficult, yet it is significant that the order of the maxima obtained by Konovalov<sup>46</sup> for aniline and its methyl-substituted derivatives with acetic acid parallels the order of the dissociation constants of these bases<sup>47</sup> in aqueous solution (*i. e.*, methyl aniline > aniline > dimethyl aniline). With the much stronger arylamines (amylamine and isobutyl amine) and acetic acid, Patten<sup>48</sup> obtained specific conductivity curves showing *two distinct maxima*, one on either side of the equimolecular mixture, which thus exhibits a *minimum* conductivity. The diversity between the two components is here, evidently, sufficiently pronounced to induce the formation in quantity of compounds more complex and ionically much more unstable than the simple equimolecular compound. An exactly similar curve is given by a more familiar system of the same type, sulfuric acid:water,<sup>49</sup> a minimum specific conductivity corresponding with the stable equimolecular compound,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . Methyl and ethyl alcohols with hydrogen chloride may be cited as additional examples, already discussed from the same viewpoint by Maass and McIntosh.<sup>50</sup>

### Compound Formation and Electro-affinity.

The results of the present article may also be interpreted—reversing for the moment the sequence of the argument—as justifying the tacit assump-

<sup>45</sup> Rivett and Sidgwick, *J. Chem. Soc.*, 97, 734 (1910).

<sup>46</sup> Konovalov, *Wied. Ann.*, 49, 733 (1893).

<sup>47</sup> Landolt-Börnstein, "Tabellen," 1912, p. 1179.

<sup>48</sup> Patten, *J. Phys. Chem.*, 6, 554 (1902).

<sup>49</sup> Kohlrausch, Landolt-Börnstein, "Tabellen," 1912, p. 1099.

<sup>50</sup> Maass and McIntosh, *THIS JOURNAL*, 35, 535 (1913).



tion made throughout this series that the "diversity factor" for the constituent groups in *non-aqueous* solutions may be postulated directly from the results obtained by comparison of acidic (or basic) strengths or by differences in electrode potentials in *aqueous* solutions. It has been demonstrated here, for example, that trichloro-acetic acid is much stronger than acetic acid not only in water, but in other basic solvents such as ketones and esters.<sup>51</sup> When acetic acid is employed as a solvent, an acid of similar strength in aqueous solution (propionic acid) is practically a non-electrolyte, while stronger acids (monochloro-acetic, trichloro-acetic) and bases (formamide, water, aniline, amyl amine) give increasingly greater specific conductivities the greater the divergence in character exhibited by the variable group in aqueous solutions.<sup>52</sup> We can therefore deduce the general rules that the order of the electro-affinities of different radicals is substantially the same whatever the solvent, and that increasing diversity in the electro-affinities of the constituent groups runs parallel to association in pure liquids, to compound formation in binary solutions, and to ionization in both.<sup>53</sup>

### Summary.

The complete specific-conductivity—composition curves for 14 systems of the types: acid:ester, acid:ketone, acid:acid and acid:base have been determined with the greatest possible degree of accuracy. New standards of purity (as demonstrated by lowering of accepted specific-conductivity values) have been set for the majority of the substances employed.

The conductivities of solutions of the above types are, in general, considerably in excess of those of the pure components, and increase uniformly with increasing diversity in character (*i. e.*, in the positive or negative nature of the constituent radicals) of their components. The results here obtained have been correlated with those derived from freezing-point measurements upon similar systems, and the validity of the fundamental relationships between compound formation and ionization in solutions, postulated in the preceding article, has been confirmed.

In subsequent papers the viscosity curves for the above systems will be presented and the theoretical discussion continued.

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<sup>51</sup> See also Walker, McIntosh and Archibald, *J. Chem. Soc.*, 85, 1098 (1904).

<sup>52</sup> See also Walden, *Trans. Faraday Soc.*, 6, 71 (1910).

<sup>53</sup> Compare Kendall, *Proc. Nat. Acad. Sci.*, 7, 56 (1921). Apparent exceptions to these rules will be noted and discussed in a subsequent paper.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

## NOTES ON SILVER BROMATE.

By J. H. REEDY.

Received January 13, 1921.

**Variation in Potential.**—In a study of silver electrodes which the writer made a few years ago, it was noticed that the potential of the electrode  $\text{Ag} | \text{solid AgBrO}_3 | 0.1 \text{ M KBrO}_3$ , when freshly prepared, was not definite, but underwent a progressive change for some time. This change frequently amounted to more than 100 millivolts, and was always in the direction indicating a decrease in the solubility of the silver bromate. The silver bromate used was of "technical" grade, and according to the statement of the manufacturers, was made by the action of an excess of bromine on silver nitrate solution. Its composition was therefore a mixture of silver bromate and silver bromide in the molar ratio 1:5. Representative results (referred to the 0.1 *N* calomel electrode as +0.342 volt) are given in Table I, the temperature being 25°. In all cases, the electrode, upon standing, finally gave a value of +0.631 volt.

TABLE I.—VARIATION IN THE ELECTRODE  $\text{Ag} | \text{AgBrO}_3$  IN 0.1 *M*  $\text{KBrO}_3$ .

Time, days.	Electrode potential. Volt.
0	+0.795
1	+0.643
2	+0.641
3	+0.634
4	+0.631
5	+0.631

**Purification.**—To meet the possibility that this change of potential might be due to the presence of some metastable substance in the impure silver bromate, this material was purified by extraction with hot water, using the apparatus shown in Fig. 1. The recrystallized silver bromate was collected on a filtering plate P, washed several times with ice water, and finally dried in a vacuum desiccator. Silver bromate prepared in this way is pure white, and appears when dry to be wholly unaffected by light. The wet salt was not found to be so stable.<sup>1</sup> A portion of the pure material was placed in a carefully cleaned tube, covered with water, and the top of the tube sealed off. After standing several weeks, the side next to the window showed a slaty-gray color, while the rest was only slightly affected. To see if there was any change in volume during the darkening, due to the formation of an insoluble gas (oxygen, supposedly), some wet silver bromate was sealed in a tube with a manometer containing pure liquid paraffin attached. After standing for more than a year there was no displacement of the levels in the arms, as shown by a "blank"

<sup>1</sup> Cf. Stas, *Mem. de l'Acad. r. de Belgique*, 35, 82, 118.

apparatus alongside. This darkening effect is very marked when wet crystals are heated, though the dry salt seems to be quite stable. Instead of decomposing about  $150^{\circ}$ , as was reported by Stas, the carefully

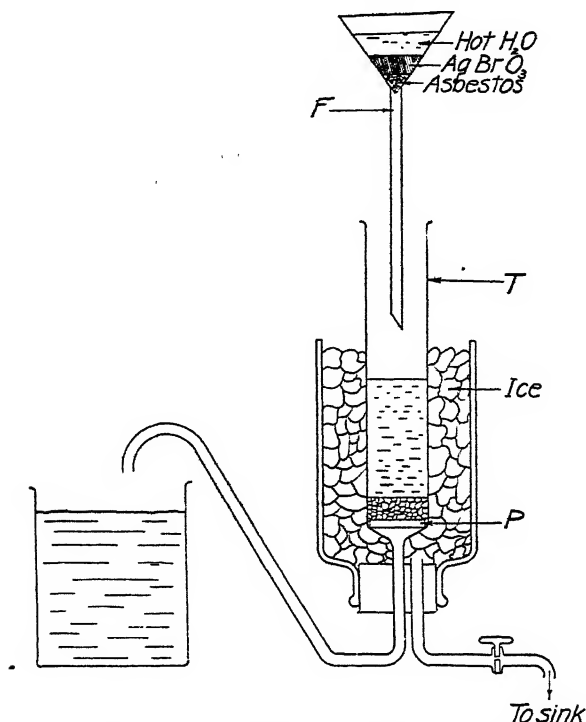


Fig. 1—Recrystallization of silver bromate.

purified salt was heated above its melting point ( $308$  to  $310^{\circ}$ ) without visible decomposition. The introduction into the heated salt of a foreign substance, as a little dust, was found to cause violent explosion.

The purity of the recrystallized product was determined as follows. Samples were weighed in evaporating dishes and converted into silver bromide by evaporation to dryness with an excess of pure hydrobromic acid solution and dried at  $120^{\circ}$  to  $125^{\circ}$ . The weight of the silver bromide residue indicated degrees of purity varying slightly with the batch of crystals used. The purity usually ranged from 99.6% to 99.8%, though in one case, when the sample had been heated to  $130$ – $135^{\circ}$  for several hours, a purity of 100% was found. This deviation from absolute purity might possibly be due to the presence of a small amount of the unknown silver perbromate; however, the most natural assumption is that the foreign substance is water. This was the opinion of Stas, who reported that the last traces of water in silver bromate could not be driven off below its decomposition point.

**Dimorphism.**—Potential measurements made on electrodes using the purified silver bromate gave even more erratic results than the crude

silver bromate-bromide mixture. On the other hand, silver bromate prepared by the interaction of silver nitrate and potassium bromate solutions at ordinary temperatures gave the potential of  $+0.631$  volt immediately. It was noticed at this point that there was a difference in the crystalline form of the silver bromate prepared from hot and cold solutions. The crystals formed by sudden cooling were hair-like, while those from the cold solutions were tetragonal crystals. Figs. 2 and 3 are from microphotographs of these forms. The habit of the hair-form in

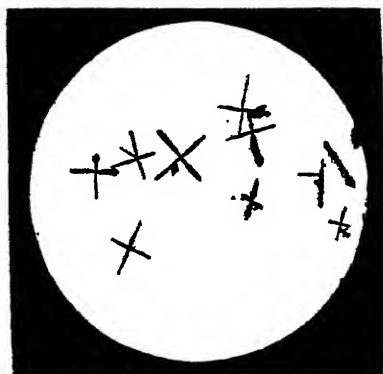


Fig. 2.—The hair form.

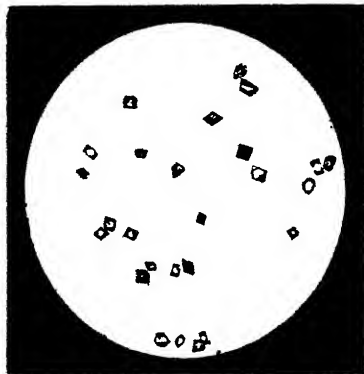


Fig. 3.—The tetragonal form.

forming crosses as shown in the figure is the frequent, but not the universal behavior of these crystals. Upon slow cooling of a hot saturated solution, however, the tetragonal form was the main product. While the hair-form is truly stable only at high temperatures, by sudden cooling (that is, "freezing the equilibrium") it may be carried over in a metastable condition into the region of the tetragonal form. In the dry condition this metastable form seems to persist indefinitely, and even in solution the reversion into the common form may be surprisingly slow. As a result of the greater solubility of the hair-form, electrodes whose solutions contain it show elevated potentials. The fact that Retgers<sup>2</sup> has already pointed out that silver chlorate shows the phenomenon of dimorphism had been assumed by the writer as presumptive evidence that the bromate also might crystallize in two forms.

**Solubility and Transition Point.**—At the suggestion of the writer, Mr. S. J. Gould has determined the solubility curve for silver bromate in water and the transition point of the two forms.

Samples of saturated solutions were taken at various temperatures between  $25^{\circ}$  and  $100^{\circ}$ , and weighed in glass-stoppered bottles. Due precautions were taken against change in concentration owing to cooling

<sup>2</sup> Retgers, *Z. physik. Chem.*, 5, 438 (1890).

during the transfer. After cooling and weighing, the amount of silver bromate was determined by adding an excess of potassium iodide solution, acidifying with dil. hydrochloric acid, and titrating the liberated iodine with standard thiosulfate solution. Table II shows the solubilities as

TABLE II.—SOLUBILITY OF  $\text{AgBrO}_3$ .

Temperature. ° C.	Solubility in 100 g. of $\text{H}_2\text{O}$ . G.
25	0.196
30	0.227
35	0.269
40	0.316
45	0.371
50	0.433
55	0.497
60	0.570
65	0.648
70	0.735
75	0.832
80	0.936
85	1.055
90	1.325

read from the curve and Fig. 4 the curve itself.

The solubility value for the stable form at  $25^\circ$  has been confirmed by e. m. f. measurements. Since there is some doubt as to the exact value of the normal silver electrode, a cell of the concentration type is desirable for this work. The combination used was  $\text{Ag}[\text{AgBrO}_3|\text{solid } 0.1 M \text{ KBrO}_3 \text{ sat. w. AgBrO}_3|\text{Conc. KNO}_3|0.1 M \text{ AgNO}_3|\text{Ag}]$ . This cell gave a potential of 0.1193 volt at  $25^\circ$ . Assuming that the onization of 0.1  $M$  potassium bromate solution is 82.5%, and of saturated silver bromate solution in 0.1  $M$  potassium bromate solution is 98% (the same as for potassium bromate and silver nitrate at the corresponding concentration), a solubility of 0.00827 mole per liter, or 0.1955 g. per 100 g. of water, is indicated.

No indication of a break in the solubility curve appears until near the boiling point of the

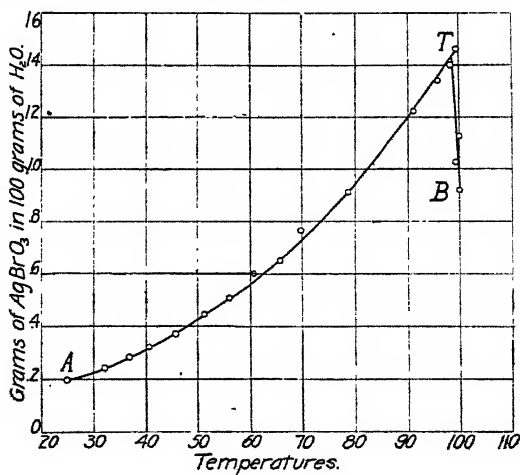


Fig. 4.—The solubility of silver bromate.

solution, where some apparently irregular values are found. The stations on the curve *BT* (Fig. 4) were obtained from solutions which had been allowed to boil for some time, the samples being taken after slight cooling. Evidently these values are somewhat uncertain. High confidence is placed in the values given in the curve *AT*. Solubility data may be said to indicate a transition point near  $98.5^{\circ}$ , with a possible error of  $0.5^{\circ}$ .

The dilatometer method gave practically the same value for the transition point. A saturated hydrocarbon oil of high boiling point, obtainable

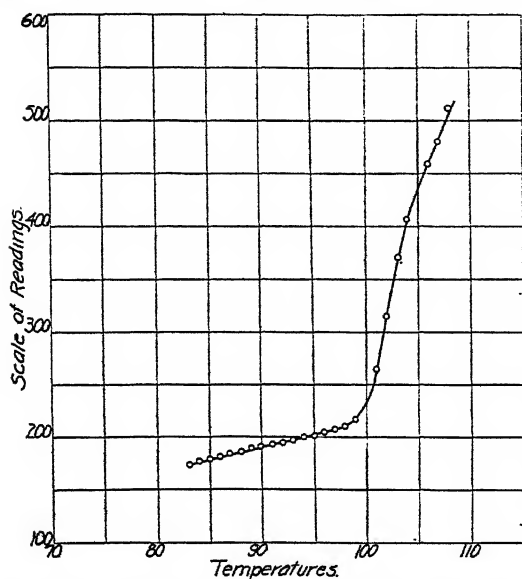


Fig. 5.—Dilatometer readings for silver bromate in "Nujol."

commercially, was used as the liquid. Readings are plotted in Fig. 5, and a transition point of about  $98.5^{\circ}$  is again indicated. The apparent break in the curve at about  $104^{\circ}$  is due to the fact that a gas begins to be evolved near that point.

**A Standard in Iodimetry.**—In view of the stability of silver bromate and the ready determination of its purity, its suitability as a standard in iodimetry suggests itself, and was investigated in the following way. The purity of the silver bromate used was determined

by converting it into silver bromide by the hydrobromic acid treatment described above. Samples of approximately one g. each were weighed into 250 cc. volumetric flasks, 150 cc. of water and an excess of potassium iodide added and the mixture was heated for some time on a steam-bath. In this way the silver bromate is completely converted into silver iodide and potassium bromate. The contents of the flask were then cooled and made up to 250 cc. Samples of 25 cc. each were acidified with dil. hydrochloric acid and titrated with sodium thiosulfate solution. The usual arsenious oxide method, using the highest grade of arsenic trioxide available, gave a titer appreciably higher than the silver bromate, *viz.*, 0.2%. This indicated that the purity of the silver bromate was greater than that assumed, or that the purity of the arsenic trioxide was less than 100%. Later, after recrystallizing the arsenic trioxide from dil. hydrochloric acid solution and subliming

it very carefully at as low a temperature as possible so as to prevent decomposition into metallic arsenic and oxygen, results were obtained which checked with the silver bromate within 0.05%. This indicates that while silver bromate may have a somewhat higher oxygen equivalent than arsenic trioxide, this defect is fully compensated by its greater definiteness.

**Gas Evolved upon Heating.**—It was noticed that a gas was evolved when silver bromate was heated in contact with water to about 100°. The same thing was found in the dilatometer determination in which the liquid medium was a saturated paraffin oil. The gas was assumed at first to be oxygen in the first case, and oxygen or carbon dioxide in the second. The fact that there was no sensible change in the composition of the silver bromate led to a closer investigation of this phenomenon. An apparatus was devised for heating the salt in contact with these liquids and catching the gas evolved. An atmosphere of hydrogen was kept above the liquids so as definitely to exclude air. The gas in both cases turned out to be a mixture of oxygen and nitrogen in practically the proportion occurring in the atmosphere. Spectroscopic examination gave no evidence of anything else. In the case of water as the liquid, 1 gram of silver bromate yielded during heating for 3 or 4 weeks at 90 to 100° slightly more than 4 cc. of gas. With the oil it gave a little less. It is supposed that the air was occluded during the precipitation of the crystals, or else absorbed later. The latter supposition is favored by the fact that the silver bromate was always precipitated from hot solutions.

This absorbed air suggests an alternate theory for the deviation of the purified silver bromate from 100% purity. The weight of the 4 cc. of air absorbed by one gram of the salt would amount to an impurity of about 0.5%, just as found above.

### Summary.

1. Silver bromate exists in dimorphic forms, *viz.*, tetragonal pyramids, stable at ordinary temperatures, and hair-like crystals, stable near 100°.
2. The variations in the potential of silver bromate electrodes are due to the presence of the metastable hair-like form, which shows a higher solubility than the tetragonal form.
3. Dry silver bromate is stable toward light and heat, but in the presence of water darkens slowly at low temperatures, and rapidly at high temperatures.
4. Silver bromate may be used as a standard in iodimetry.
5. Silver bromate crystals absorb an appreciable amount of air which is slowly given up at high temperatures.

[JOINT CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ARIZONA AND NEW HAMPSHIRE COLLEGE.]

## THE RATES OF HYDROLYSIS OF THE RARE EARTH CARBONATES AND THE SERIAL ORDER OF THE RARE EARTH ELEMENTS.

BY PAUL H. M.-P. BRINTON AND C. JAMES.

Received February 14, 1921.

### Introduction.

If the elements of the rare earth group are arranged in the order of increasing atomic weights, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, (Y), Er, Tm, Yb, Lu, Ct, it is found that in general this series represents the order of progressive variation in a number of other properties of the compounds of these elements. This *Serial Order*, as it is called, represents the order of solubilities of many series of rare earth salts, and therefore, usually, the order in which the compounds of the elements separate from solution in the operations of fractional crystallization. The order of decomposition of the nitrates on heating, and the order of precipitation by gradual addition of hydroxyl ion are also in general harmony (inversely) with this series, so that the series seems to represent the order of decreasing basicity of the elements.

A number of inconsistencies exist, however. Thus yttrium, with an atomic weight far below that of lanthanum, is placed, by general considerations of the solubilities of its compounds, between holmium and erbium; while the order of precipitation by ammonium hydroxide shows that its relative basic strength places it about with neodymium. Measurements of the dissociations of the anhydrous sulfates<sup>1</sup> indicate a degree of basicity for yttrium second only to that of lanthanum, admittedly the most strongly basic of the rare earths. By this same method samarium is given a place between gadolinium and terbium, and by fractional precipitation with ammonium hydroxide<sup>2</sup> samarium falls in the same position. Solubility considerations, on the other hand, place samarium between neodymium and europium in the serial order; and this same position has been accorded samarium by a study of the hydrolysis of sulfates.<sup>3</sup>

With a view to securing further data on the relative basicities and the serial order of the rare earth elements we have studied the rates of hydrolysis of the carbonates of 12 of these elements. In briefest outline,

<sup>1</sup> Wöhler and Gründzweig, *Ber.*, 46, 1726 (1913).

<sup>2</sup> de Boisbaudran, *Compt. rend.*, 111, 393 (1890); Benedicks, *Z. anorg. Chem.*, 22, 398 (1900).

<sup>3</sup> Katz and James, *THIS JOURNAL*, 36, 779 (1914).



the method was to prepare accurately standardized solutions of the rare earth sulfates, to add equivalent amounts<sup>4</sup> of each sulfate solution to separate portions of 0.5328 g. of purest sodium carbonate, and to heat for given lengths of time, under carefully controlled temperature conditions. The carbon dioxide resulting from the hydrolysis was weighed. Volume, and other conditions were maintained as uniform as possible in all experiments.

### Preparation of Materials.

The methods of separation and purification of the compounds of the various elements considered in this paper have been described elsewhere,<sup>5</sup> and need not be repeated here.

The method of preparing the sulfate solutions was the same for all the solutions. The oxide finally obtained from ignition of the purest oxalate was dissolved in the smallest possible amount of hydrochloric acid. Slightly more than the theoretical amount of sulfuric acid was then added to the somewhat diluted solution, and this was then poured into a large excess of 95% ethyl alcohol. The precipitated sulfate was thoroughly washed with alcohol, and dehydrated by heating to 280–300°. The anhydrous sulfate thus obtained was dissolved in ice-cooled water. By evaporating to small volume in a bath of boiling water the hydrated sulfate was deposited in crystalline form. The crystals were filtered, and washed repeatedly with small amounts of boiling water until no trace of acid reaction could be detected in the washings. The crystals were allowed to stand over sulfuric acid in a desiccator for a day, and then dissolved in carbon dioxide free water to make a 0.1 *N* solution. The solution was standardized by precipitating pipetted samples as the oxalate, and igniting to the oxide,  $R_2O_3$ .

The only deviations from the above methods of standardization were the following: ytterbium was precipitated by ammonium hydroxide, owing to the considerable solubility of the oxalate; praseodymium was weighed as the oxide  $Pr_2O_3$ , after ignition in a current of hydrogen; terbium was weighed as  $Tb_4O_7$ , after ignition in the air.

Figures showing the concordance of these determinations may be replaced by the statement that the most discordant pair of the duplicates was in the case of ytterbium, which gave 0.3308 g. and 0.3301 g. of ytterbium oxide.

Sodium carbonate was prepared by saturating water at 60° with the purest sodium hydrogen carbonate of commerce. Carbon dioxide was passed into the filtered solution until cold, and the deposited sodium hydrogen carbonate was heated in platinum at 270 to 300° for several hours. 102.218 g. lost only 4. mg. on heating for 2 hours more at the same temperature; so it was heated for 1 hour after the last weighing, cooled in a desiccator over sulfuric acid, and quickly transferred to small stoppered bottles. 1.9796 g. of the sodium carbonate yielded on evaporation with sulfuric acid and gentle ignition with ammonium carbonate, 2.6547 g. of sodium sulfate. This agreed with the theoretical amount to within 4 parts in 10,000, so the sodium carbonate was considered pure enough for our purposes.

### Experimental.

The reaction chamber was a 500-cc. round-bottom flask with a neck

<sup>4</sup> Equivalent amounts of rare earth sulfate and sodium carbonate were used in order to avoid the formation of double carbonates or double acid salts. Such compounds as these are very characteristic of the rare earth metals.

<sup>5</sup> Vid. James and co-workers, *ibid.*, 1907 to date.

15 cm. long. Through one hole of the stopper a glass tube passed almost to the bottom of the flask, and the outer end of this tube could be connected with a funnel for the introduction of liquid, or with a large soda-lime tower for the purification of incoming air. Through the other hole of the stopper a 24-cm. bulb condenser was vertically set. Following the condenser was a train consisting of a large U-tube filled with sulfuric acid, a long horizontal calcium chloride tube, a Geissler potash bulb with a calcium chloride guard tube, and then another sulfuric acid tube, beyond which was the aspirator bottle.

The heating was accomplished by a gas flame 7.5 cm. high, with an inner cone 2.5 cm. high. The bottom of the flask was 4 cm. above the top of the burner. All draughts were excluded, and a pressure-equalizing tank between the burner and the main gas supply insured uniformity of flame.

In making a run, exactly 0.5328 g. of sodium carbonate was rinsed into the flask with 25 cc. of water. (All water used in these experiments was previously freed from carbon dioxide by boiling, and then cooled with the usual precautions.) The flask and train were then freed from carbon dioxide by aspirating several liters of pure air through. Next, the weighed potash bulb was placed in the train, and an amount of rare earth sulfate solution chemically equivalent to the sodium carbonate was introduced through a funnel attached to the tube leading to the bottom of the reaction flask, and this was rinsed with enough water to give a volume of 229.12 cc. This volume, and the weight of sodium carbonate were empirical, resulting from the experimental conditions of the first run, and maintained as standard throughout the series. The funnel was disconnected, the large soda-lime tower connected in its place, and aspiration was then started at the rate of 2.5 liters per half-hour. The flame was next placed under the flask, and the heating continued for exactly 30 minutes after incipient ebullition. The flame was then turned out and the "sweeping" with pure air continued for exactly 20 minutes. The potash bulb was weighed with the usual precautions, placed back in the train, the boiling and "sweeping" being repeated exactly as before. This operation was usually repeated 6 to 8 times with each sample, and the percentage hydrolysis calculated for each half-hour boiling period. Duplicates were run on all the elements considered in this paper with the exception of europium, terbium, and thulium, of which we had amounts sufficient for one run only.

Below are given the results of the experiments, giving the percentage hydrolysis, (*i. e.*, the amount of carbon dioxide given off, divided by the total carbon dioxide originally present in the system), at the end of each half-hour period.

Hours of Boiling:	0.5.	1.0.	1.5.	2.0.	2.5.	3.0.	3.5.	4.9.
$\text{La}_2(\text{CO}_3)_3$								
%Hydrolysis, 1st sample	27.9	27.9	28.0					
2nd "	27.5	27.5	27.6					
3rd "	28.1	28.3	28.3					
Average	27.9	27.9	28.0					
$\text{Ce}_2(\text{CO}_3)_3$								
	28.5	28.5	28.7					
	29.3	29.4	29.4					
	28.9	28.9	29.0					
$\text{Pr}_2(\text{CO}_3)_3$								
	22.4	26.7	28.8	29.9	31.2	32.1	33.2	
	24.0	28.0	30.1	31.8	32.6	33.1	33.5	
	23.2	27.4	29.5	30.9	31.9	32.6	33.3	
$\text{Nd}_2(\text{CO}_3)_3$								
	26.8	30.2	32.7	34.3	35.4	36.4	36.9	
	26.3	30.4	32.6	34.4	35.5	36.4	37.2	
	26.6	30.3	32.7	34.4	35.5	36.4	37.1	
$\text{Sm}_2(\text{CO}_3)_3$								
	30.8	34.7	37.2	39.2	40.8	42.2	43.4	44.2
	32.0							
	32.6	36.0	38.4	39.8				
	31.8	35.4	37.8	39.5	40.8	42.2	43.4	44.2
$\text{Eu}_2(\text{CO}_3)_3$								
	33.4	37.4	39.9	41.9	43.6	45.1	46.3	47.0
$\text{Gd}_2(\text{CO}_3)_3$								
	35.0	39.4	41.9	43.7	45.3	46.3	47.4	48.3
	34.6	38.4	40.7	42.5	43.5	45.0	46.1	46.9
$\text{Tb}_2(\text{CO}_3)_3$								
	34.8	38.9	41.3	43.1	44.4	45.6	46.7	47.6
	37.6	42.5	45.7	48.1				
$\text{Dy}_2(\text{CO}_3)_3$								
	39.4	43.6	46.8					
	40.6	45.3	48.5	50.7	52.2	53.4		
	40.0	44.4	47.6	49.9	51.4	52.8		
$\text{Y}_2(\text{CO}_3)_3$								
	46.8	50.6	53.4	55.3	56.0	57.0		
	43.0	46.5	48.5	50.3	51.9	53.1		
	44.9	48.5	51.0	52.8	54.0	55.1		
$\text{Tm}_2(\text{CO}_3)_3$								
	49.0	53.1	55.5	57.5	59.3			
$\text{Yb}_2(\text{CO}_3)_3$								
	52.6	57.3	60.4	62.4	64.4	66.1	67.3	68.5

The degree of accuracy of the individual determinations may be judged by the concordance in the results of analyses of the duplicate samples. While the concordance is not as close as might be desired in certain classes of measurements, yet it seems fair to assume that the position of an element in this series is not rendered doubtful by the limitations of the experimental methods used. Thus it will be seen that in the first (which

is the most important) stage of each run the highest figure for one element is lower than the lowest figure of the next higher element.

The results are graphically shown in Fig. 1, in which the percentages hydrolyzed are plotted against the time of boiling.

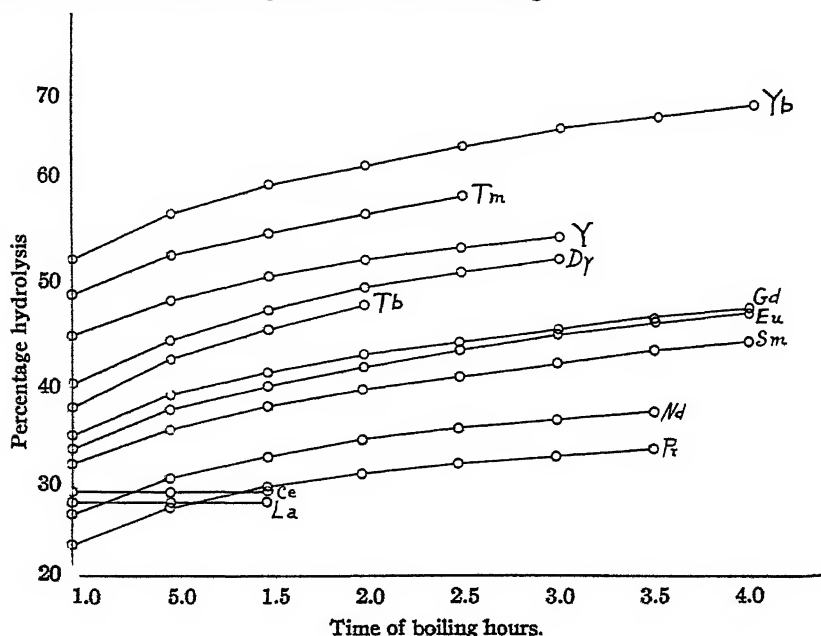


Fig. 1.

### Discussion of Results.

The behavior of lanthanum and cerium<sup>III</sup> is abnormal in comparison with the others. Hydrolysis seems to reach its limit in the first half-hour with these elements, while with the others there is a continuous, gradually decreasing amount for each additional period of boiling. That cerium should show a different behavior is not surprising, since cerium is really a fourth group element, and is not to be regarded as a "rare earth" element. Lanthanum also shows certain variations from the strict rare earth group.<sup>6</sup> It gives no absorption spectra, it finds a place in the old periodic table, and in general shows greater characteristic individuality than do the other members of the rare earth group.

The position of yttrium is interesting. General considerations of the solubilities of its compounds places yttrium between holmium and erbium, but the order of precipitation by ammonia places it about with neodymium. Our results on the hydrolysis of yttrium carbonate place the element between dysprosium and thulium, and while holmium and erbium were

<sup>6</sup> Hauser and Wirth, *Z. anal. Chem.*, 47, 395 (1908).

not available for our tests, these two also come between dysprosium and thulium in the generally accepted serial order, and it is not improbable that had we been able to investigate holmium and erbium they would have found a place on each side of yttrium. From our results the position accorded to yttrium (just below lanthanum in basicity) by Wöhler and Grünzweig<sup>7</sup> from their study of the dissociation of the anhydrous sulfates seems to be erroneous.

Hydrolysis of the carbonates places europium between samarium and gadolinium, and lends additional support to the serial order established by solubility relations. This is at variance with the order of precipitation by ammonia, as well as that indicated by the sulfate tensions investigated by Wöhler and Grünzweig.

It is worthy of note that a large space occurs in our Fig. 1 between neodymium and samarium. This is in harmony with the idea derived from study of the atomic numbers<sup>8</sup> that there is an undiscovered rare earth element with a position between those of neodymium and samarium.

### Summary.

The relative rates of hydrolysis of 12 rare earth carbonates have been determined.

Lanthanum and cerium<sup>III</sup> showed an abnormal behavior, for which no explanation can now be offered.

Yttrium has been assigned a position in the order of basicity which agrees with the solubilities of its compounds. Previous determinations of its basicity have not done this.

Additional evidence on the serial order of samarium, europium and gadolinium has been offered.

Omitting lanthanum and cerium<sup>III</sup> for the present, the other ten elements investigated are placed in the following order: Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Tm, Yb.

TUCSON, ARIZONA.  
DURHAM, N. H.

<sup>7</sup> Wöhler and Grünzweig, *Ber.*, **46**, 1726 (1913).

<sup>8</sup> Moseley, *Phil. Mag.*, **26**, 210 (1913); **27**, 703 (1914).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 133.]

## THE JOULE-THOMSON EFFECT FOR AIR.

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Received February 17, 1921.

There has recently been completed by L. G. Hoxton<sup>1</sup> a very painstaking experimental investigation of the Joule-Thomson effect in the case of air. In this investigation the effect was measured at several pressures and temperatures, use being made of the experimental values obtained to compute the position of the ice point on the absolute-temperature scale, as well as the constant-pressure air-thermometer-scale corrections to reduce gas-scale readings to the absolute scale. From the temperature coefficient of the Joule-Thomson effect the pressure coefficient of the specific heat for air was computed and compared with the experimental value found by Holborn and Jacobs.<sup>2</sup>

For the absolute temperature of the ice point 273.36 was obtained, while the constant-pressure air-thermometer corrections were in agreement with the mean of the corrections arrived at by Rose-Innes, Callendar, Berthelot, and Buckingham for the nitrogen thermometer. The pressure coefficient of the constant-pressure specific heat for air computed from the temperature coefficient of the Joule-Thomson effect is moreover in good agreement with the first pressure coefficient of Holborn and Jacobs' empirical equation based on their experimental values.

The attention given to possible sources of error and in fact to all details of the experimental procedure by Hoxton is such as to make the work a most important contribution to the experimental study of the Joule-Thomson coefficient. The values obtained, nevertheless, are higher than those obtained by previous workers as noted by Hoxton, and, in consequence, lead to a higher value of the ice point (273.36) than that arrived at by other methods. Hoxton indeed calls attention to the fact that in general the use of the Joule-Thomson effect in computing this constant has, in the calculations of everyone, led to a high value. Thus Buckingham<sup>3</sup> found for the absolute ice-point temperature, making use of the respective Joule-Thomson effects, for air 273.273, for nitrogen 273.286, for carbon dioxide 273.267, while in the case of hydrogen 273.049 was obtained. Berthelot,<sup>4</sup> however, making use of a method of computation based on his equation of state concluded that 273.09 was the correct ice-point temperature, and recently there were presented the results of some calculations by means

<sup>1</sup> Hoxton, *Phys. Rev.*, **13**, 438 (1919).

<sup>2</sup> Holborn and Jacobs, *Z. Ver. deut. Ing.*, **58**, 1429 (1914).

<sup>3</sup> Buckingham, *Bur. Standards, Bull.* **3**, 237 (1907).

<sup>4</sup> Berthelot. *Trav. Nem Bur. Int.* **13**. (1907).

of my<sup>5</sup> equation of state, applied to nitrogen, hydrogen and helium in the case of both the constant-pressure and constant-volume gas thermometers, which lead to a value somewhat higher (273.14) than Berthelot gives.

In the procedure wherein use is made of the Joule-Thomson coefficients as well as in the equation of state method of arriving at the ice-point temperature, the experimentally determined constant-pressure and constant-volume coefficients of volume and pressure increase between the melting and boiling points of water must be employed. Evidently, if these coefficients were in error, the error would be carried through into the values obtained for the ice-point temperature, and, indeed, high accuracy is demanded since to obtain an accuracy of  $0.1^\circ$  in the ice-point temperature requires that the coefficients should be known to about 1 part in 27000. On the other hand, for this degree of correctness, in the case of air, it is sufficient to have approximately 1% accuracy in the Joule-Thomson coefficient which is involved in the correction term applied to the expansion coefficient.

Apropos of the extreme accuracy with which the expansion coefficient must be known, it is of interest to call attention to the importance in precise measurements of the adsorptive effect of the container walls. The discrepancies in the coefficients of expansion as measured by the same and by different observers may well be assigned to surface adsorptive effects on the inner surface of the thermometer bulb; not perhaps in general to adsorption of the gas on the envelope surface directly but to adsorption or absorption by the water layer which always attaches tenaciously to surfaces.<sup>6</sup> For example, Eumorphopoulos,<sup>7</sup> employing a quartz thermometer bulb with the Callendar compensating type of instrument, after cleaning the bulb with nitric acid and mixed chromic and sulfuric acids, washing repeatedly with distilled water, drying and heating to  $500^\circ$  under exhaustion, found that pure nitrogen dried by phosphoric acid admitted and re-exhausted several times, gave the coefficient of volume increase per degree per cc.  $3.671 \times 10^{-3}$  at 760 mm. Heating and loading as before reduced the value to  $3.6701 \times 10^{-3}$ . It would appear then that the difficulty of extracting adsorbed material from the walls is great even in quartz, and in fact, the gas expansion values of other observers, notably those coefficients measured in glass thermometer bulbs, are invariably high,<sup>8</sup> as compared to values obtained in metal bulbs.

<sup>5</sup> Keyes, *Proc. Nat. Acad. Sci.*, 3, 323 (1917). This equation is:  $p = RT/(v - \delta) - A/(v - l)^2$ , where  $\ln \delta = \ln \beta - \alpha/v$ .

<sup>6</sup> See also for example, concerning the weight of a liter of ammonia: "Thermodynamic Properties of Ammonia," Keyes and Brownlee, p. 216, Wiley and Sons, 1916.

<sup>7</sup> Eumorphopoulos, *Proc. Roy. Soc.*, 90A, 189 (1914).

<sup>8</sup> Holborn and Henning, *Ann. Physik.*, 35, 766 (1911). They obtained for nitrogen in 59<sup>III</sup> glass  $3.6703 \times 10^{-3}$  at 620 mm., but in quartz  $3.6684 \times 10^{-3}$ .

The purpose of the present paper is to give the results of some calculations of the Joule-Thomson coefficients based on the use of my equation of state.<sup>5</sup> The equation of nitrogen for example, has been shown to give the Amagat pressures to about 1000 atmospheres with great exactness over a range of 200°. In the case of air, as will be shown below, the pressures given by Amagat are also in good agreement as well as are the pressures given by other observers at temperatures as low as -130°, although in the latter case not high pressures for reasons which can be more appropriately discussed in another paper. It is conceivable, however, that an equation of state might serve to calculate pressures over a comparatively limited temperature range to a very satisfactory degree and still be defective in form, and in consequence lead to erroneous values for the derived quantities, such as, for example,  $\left(\frac{\partial v}{\partial T}\right)_p$  and  $\left(\frac{\partial p}{\partial T}\right)_v$  which are involved in calculating the Joule-Thomson coefficients.

The form of function has, however, been tested by comparing the term (corresponding to van der Waals'  $b$ ) and  $\phi$  the cohesive pressure term separately at high pressures over a temperature range extending 100° on each side of the fixed points (0° and 100°) under discussion in the present paper. The functional forms for  $\delta$  and  $\phi$  in the equation have been shown to be exact, and at low pressures should give accordingly the derived quantities with great precision.

To give a survey of the degree of exactness with which the equation of state for air accords with the measurements, there are presented in Tables I, II and III the data of Amagat<sup>9</sup> upon which the constants of the equation are based, those of Witkowski<sup>10</sup> and finally, the recent pressure volume and temperature observations for air by Holborn and Schultz.<sup>11</sup>

The agreement of the calculated and observed pressures is not perhaps as good as in the case of nitrogen because the oxygen of the air in Amagat's work might have reacted to some extent with the mercury used to confine it at higher temperatures and pressures. Each observer's data are, however, well represented, and the equation is, therefore, concluded to be exact from -130 to 200° over a wide pressure range.<sup>12</sup>

<sup>9</sup> Amagat, *Ann. chim. phys.*, 29, 52 (1893).

<sup>10</sup> Witkowski, *Bull. Acad. Cracovie*, 1891, 181; or *Phil. Mag.*, 41, 288 (1896).

<sup>11</sup> Holborn and Schultz, *Ann. Physik.*, 47, 1089 (1915).

<sup>12</sup> It has been suggested that any equation of state containing four constants should represent the data. The habit of regarding an equation as simply one containing a number of arbitrary constants which will represent the data with better accuracy as the number of constants is increased is certainly common enough, but not particularly adequate. In the case of an equation of state, there is a relation between three variables, and the form of the function becomes of more importance than the mere number of constants.

There are examples enough in the literature of equations having many constants



TABLE I.  
EQUATION OF STATE FOR AIR.  
Observations of Amagat.

Pressures in atmospheres of 760 mm., volumes in cc. per g.				
V.	0°.	99.4°.	200.4°.	
7.525	100.0	146.0	193.0	Observed pressure Amagat
	99.71	146.08	193.19	Calculated Eq. of state.
5.073	150.0	227.0	303.0	Obs.
	149.71	226.14	303.8	Calc.
3.906	200.0	310.0	420.0	Obs.
	200.29	309.85	421.15	Calc.
3.245	250.0	395.0	538.0	Obs.
	250.50	394.28	540.37	Calc.
2.829	300.0	479.0	655.0	Obs.
	298.81	476.25	656.55	Calc.
2.550	350.0	564.0	770.0	Obs.
	349.51	560.77	775.42	Calc.
2.348	400.0	646.0	881.0	Obs.
	403.07	646.05	892.93	Calc.
2.194	450.0	728.0	993.0	Obs.
	443.50	717.23	995.23	Calc.

$$p = \frac{2.833}{v - \delta} T - \frac{A}{(v - l)^2}, \text{ where } \log_{10} \delta = 0.20113 - \frac{0.296}{v} \quad A = 1605.3; l = -0.088.$$

Having shown that the pressures for air are given by the equation over a wide range of pressure, volume and temperature, the Joule-Thomson coefficients calculated from the equation are valuable as a standard of reference from which to discuss the experimental values. Moreover, by means of a comparison of calculated and experimental values, some light will be thrown upon the magnitude of the possible errors affecting the expansion coefficients and the Joule-Thomson numbers, thus assisting in extending the accuracy with which these important constants can be measured.

A peculiarity of the particular equation<sup>13</sup> of state for air, so far above its critical temperature, is that the pressure at constant volume is a linear and still failing to represent the pressure, volume and temperature data as accurately as desirable. In a recent article (THIS JOURNAL, 41, 591 (1919)), I have gone into this matter at some length to make clear the importance of the form of function, and in the article referred to special measurements were made to test the functional form, and further data are being obtained with improved apparatus.

<sup>13</sup> In a previous paper (THIS JOURNAL, 41, 589 (1919)), it has been shown that the equation in the simple form is particular in that it applies to a system whose molecules remain of invariable species in a given phase. That is to say, there is assumed to be no association, which at so many degrees above the critical point is true enough for the so-called permanent gases. It is only for a one-type molecular assemblage that the linear increase of pressure with temperatures at constant volume is conceivable. Indeed, for such a system, any other manner of pressure increase appears illogical unless we are



function of the temperature. In the region of the critical temperature and of small volumes (10 cc. per g.), this is no longer true. The linear increase of pressure with temperature at constant volume requires as a thermodynamic consequence that the constant-volume specific heat shall be independent of the volume. The constant-pressure specific heat  $C_p$  will, therefore, follow from the thermodynamic equation  $C_p =$

$C_v + T \left( \frac{\partial v}{\partial T} \right)_p \left( \frac{\partial p}{\partial T} \right)_v$  on applying the equation to compute the expression for the second term of the right-hand member. There is obtained from

$$\left( \frac{\partial p}{\partial T} \right)_v = \frac{R}{v - \delta} \quad \text{and} \quad \left( \frac{\partial v}{\partial T} \right)_p = \frac{v - \delta}{T} \times \frac{1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3}}{1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3}}$$

and the air constants, the following equation,

$$C_p = C_v + \frac{R}{1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3}} = \left[ 0.241 + 2.5 \times 10^{-4} p \right]_{58^\circ} \text{approximately.}$$

Holborn and Jacobs<sup>14</sup> find  $2.86 \times 10^{-4}$  for the pressure coefficient in their equation  $C_p = 0.2413 + 2.86 \times 10^{-4} p + 5.0 \times 10^{-8} p^2 - 1.0 \times 10^{-9} p^3$ . At 200 atmospheres the calculated specific heat is 0.291 as compared with Holborn and Jacobs' 0.2925 from the equation representing their measurements.

The thermodynamic equation of the Joule-Thomson effect is  $\frac{dT}{dp} =$

$$\mu = - \frac{T \left( \frac{\partial v}{\partial T} \right)_p - v}{C_p} \quad \text{and the equation of state gives then}$$

$$\frac{\frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3} v - \delta \left( 1 - \frac{\alpha}{v} \right)}{C_v \left( 1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3} \right) + R}$$

willing to accept that temperature can influence the residual electro-magnetic fields which are the assumed cause of the mutual attraction between the molecules composing the fluid, and such a temperature effect has not been established so far as known.

<sup>14</sup> The coefficients to the higher powers have been omitted since the first pressure coefficient of Holborn and Jacobs' empirical equation is the most accurate. In the equation given, the  $p$  coefficient is taken as  $R \times \frac{2A}{R^2 T^2}$  being the first approximation of

$$\frac{R}{1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3}} \quad \text{it being assumed that the specific heat at one atmosphere is } C_p + R = 0.238.$$

The equation given is complete, but for the low pressures that are here to be considered, it suffices to make the following reductions. For  $\frac{(v-\delta)^2 v}{(v-l)^3}$ , may be written  $\left(1 - \frac{2\beta}{RT} p\right)$ ; for  $\delta \left(1 - \frac{\alpha}{v}\right)$ ,  $\beta \left(1 - \frac{2\alpha}{RT} p\right)$ ; and for  $\frac{(v-\delta)^2}{(v-l)^3} \frac{p}{RT}$ .

There results then the equation

$$\mu_p = \mu_0 + \left[ \mu_0 \frac{C_p}{C_{p_0}} \frac{2A}{R^2 T^2} - \frac{4A\beta}{C_{p_0} R^2 T^2} + \frac{2\alpha\beta}{C_{p_0} RT} \right] p.$$

where  $\mu_0$  represents the quantity  $\left(\frac{2A}{RT} - \beta\right)/C_{p_0}$ , the Joule-Thomson effect at infinitely low pressure, and  $C_{p_0} = C_p + R$ , the constant-pressure specific heat at infinitely low pressures. It will be observed that the pressure coefficient can be positive or negative depending upon the temperature, although it is to be observed that the coefficient of  $p$  is the tangent to the  $\mu, p$  curve at the  $\mu$  axis only.

TABLE IV.  
Experimental and Computed Joule-Thomson Coefficients for Air.

$t$	Calculated.	J. and T. Buckingham.	Noell.	Hoxton.			
	1 atm.	1 to 6 atm.	Corr. states.	1 to 3 atm.	1.3 atm.	3.4 atm.	4.9 atm.
0°	0.2615	0.275	0.284	0.277	0.303	0.284	0.272
50°	0.1957	0.197	0.205	0.185	0.226	0.211	0.205
100°	0.1477	0.147	0.161	0.125	0.170	0.160	0.154

The temperature coefficient may be positive or negative depending on the temperature. The effect itself ( $\mu$ ) is zero at low pressures when  $T = \frac{2A}{R\beta}$ , but the temperature of inversion diminishes as the pressure increases at high pressures.

Substituting the numerical values of the constants given under Table I, there results the following equation,  $\mu_0 = \frac{115.8}{T} - 0.1625$  where  $C_{p_0} = 0.238$  is assumed constant. The pressure coefficient is at 0°;  $-4.7 \times 10^{-4}$  and at  $-100$ ;  $+9.2 \times 10^{-4}$  for low pressures. The mean pressure coefficient 0 to 200 atmospheres is  $7.1 \times 10^{-4}$  at zero degrees.

Table IV gives a survey of the experimental values together with those computed by the equation. It is perceived that the values of the effect obtained by Hoxton at the higher pressures are not far from those obtained by Joule and Thomson. The Joule and Thomson numbers were obtained by expanding from about 6 atmospheres down to 1 atmosphere, and, therefore, represent the integrated effect over the pressure drop.

The differences in the various values are, however, so great and the pressure effect so small ( $-4.7 \times 10^{-5}$  per atmosphere calculated for low pressures) that for the accuracy attained it is futile to take into account whether the pressure amounted to one or several atmospheres. It is to be noted, however, that Hoxton has observed a large pressure effect experimentally amounting to  $5.6 \times 10^{-3}$  or the order of ten times the calculated value ( $4.7 \times 10^{-4}$ ). Vogel's<sup>15</sup> pressure coefficient ( $8.6 \times 10^{-4}$ ) is lower than Hoxton's, but somewhat larger than that calculated, while Dalton<sup>16</sup> working in Onnes' laboratory finds  $6.0 \times 10^{-4}$ . Bradley and Hale,<sup>17</sup> however, made a series of measurements at temperatures from 0 to  $-110^\circ$  expanding through pressure differences of 68, 102, 136, 170 and 204 atmospheres to one atmosphere, thereby obtaining the integral Joule-Thomson effect.

Bradley and Hale measured the fall in temperature attending the throttling of air from 68, 75, 101, 150 and 204 atmospheres to one atmosphere when the gas on the high pressure side of the plug was maintained at a series of different temperatures. By plotting the pressures with the attendant temperature drops, a series of curves was described, one for each initial temperature. The tangent at any point on the curves is the value of  $dt/dt$  the Joule-Thomson coefficient. From the curves of Bradley and Hale's data the values at the pressures of 50, 100, 150 and 200 atmospheres were read. Each of these constant-pressure series of values was then plotted with the reciprocal of the corresponding absolute temperature, which permitted the value of  $\mu$  at the ice point to be read corresponding to each constant pressure. These ice-point temperature values are:  $\mu = 0.2330$  at 50 atmospheres,  $\mu = 0.1915$  at 100 atmospheres,  $\mu = 0.1615$  at 150 atmospheres, and  $\mu = 0.1166$  at 200 atmospheres. The values are related to the pressure with sufficient exactness for the present purpose by the equation  $\mu = 0.268 - 7.3 \times 10^{-4}p$ . This equation gives for  $\mu$  at 50 atmospheres 0.232, at 100 atmospheres 0.194, at 150 atmospheres 0.158, at 200 atmospheres 0.121. At  $0^\circ$ , therefore, Bradley and Hale's work indicates that the pressure coefficient of the Joule-Thomson effect is  $-7.3 \times 10^{-4}$ . The complete equation for the effect at zero degrees derived from the equation of state gives at 200 atmospheres 0.1196 while the one atmosphere value is 0.261. The average coefficient is therefore  $7.1 \times 10^{-4}$  which agrees very well with the Bradley and Hale value.<sup>17</sup> At low pressures the pressure coefficient is the order of  $5 \times 10^{-4}$ , so that the numerical value of the coefficient increases slowly with pressure. It appears, therefore, that the pressure coefficient as found by Hoxton is the order of 8-fold too large.

<sup>15</sup> E. Vogel, Landolt-Börnstein, "Tabellen," p. 786, 4th edition.

<sup>16</sup> Dalton, *Comm. Phys. Lab. Leiden*, 1909, 109a and 109c.

<sup>17</sup> Bradley and Hale, *Phys. Rev.*, 29, 258 (1909).

### The Expansion Coefficients of a Gas.

The computation of the expression giving the constant-pressure expansion coefficient may be readily obtained from the equation of state. For the large volumes which are here in question, it suffices to assume

$\delta = \beta$  and to neglect  $l$  in the cohesive pressure term  $\phi = \frac{A}{(v-l)^2}$ . The

equation assumes the form, therefore,  $p = \frac{R}{v-\beta} T - \frac{A}{v^2}$  for low pressure

analogous in form to the van der Waals equation. Setting  $p + \frac{A}{v^2} = \pi$

and  $(v - \beta) = \omega$  the equation of an actual gas at not too small volumes becomes  $\pi\omega = RT$  identical in form with the perfect gas equation. If  $\pi$  can be kept constant, therefore, the absolute centigrade temperatures will be given by the expression

$$t_a = \left[ \frac{\omega_t - \omega_o}{\omega \epsilon} \right]_{\pi} \quad (1)$$

where  $\epsilon$  is the expansion coefficient of a perfect gas. The quantity  $\omega_o$  will always be invariable in magnitude in a given apparatus filling, but  $\omega_t$  must be always taken with  $\pi$  or  $(p_1 + \phi_1)$  constant. Since, however, the volume is increasing with temperature rise,  $\phi$  will diminish progressively, and since  $(p_o + \phi_o)$  must always equal  $(p_1 + \phi_1)$ , where the zero subscripts refer to the ice-point values of the quantities designated and the numeral to the value of the quantities at any temperature, it is clear that

$p_1 > p_o$  and  $p_1 - p_o = \phi_o - \phi_1 = A \left( \frac{1}{v_o^2} - \frac{1}{v_1^2} \right)$  will therefore always remain

a positive quantity. If further  $\omega'$  is taken to represent the value of  $(v_1 - \beta)$  at the constant initial pressure  $p_o$  according to the usual constant pressure thermometer procedure,  $\omega_1$  will be given by multiplying  $\omega'_1$  by

the ratio  $\frac{p_o}{p_1}$ . Substituting then in Equation 1 there results,

$$\frac{\omega'_1 \frac{p_o}{p_1}}{\omega_o t_a} = \epsilon = \frac{\frac{v_1 - v_o}{v_o t} - \left( \frac{v'_1 - \beta}{v_o t} - \frac{\beta}{v_o t} \right) \left( 1 - \frac{p_o}{p_1} \right)}{\left( 1 - \frac{\beta}{v_o} \right) \frac{t_a}{t}} \quad (2)$$

At  $100^\circ$   $t_a = t$  and  $\frac{v'_1 - v_o}{v_o t} = \epsilon_p$  the expansion coefficient of the gas under

measurement. The value of  $\left( 1 - \frac{p_o}{p_1} \right)$  may be obtained in terms of the con-

stants of the equation, for since  $p_1 - p_o = \phi_o - \phi_1$ ;  $\left( 1 - \frac{p_o}{p_1} \right)$  may be taken

equivalent to  $\frac{A}{p_0} \left( \frac{1}{v_0^2} - \frac{1}{v_1^2} \right)$  or  $\frac{A \epsilon_p t}{R^2 T_0^2} \left( \frac{2 + \epsilon_p t}{1 + \epsilon_p t} \right) p_0$  assuming  $p v = R T$  for  $v_0$  and  $v_1$ . The equation for  $\epsilon_p$  may now be reduced to the following equation

$$\epsilon_p = \epsilon + \left[ \epsilon_p \frac{A(2 + \epsilon t)}{R^2 T_0^2 (1 + \epsilon t)} - \frac{\beta}{R T_0^2} \right] p_0 - \left[ \frac{A \beta \epsilon_p (2 + \epsilon t)}{R^3 T_0^3 (1 + \epsilon t)^2} \right] p_0^2. \quad (3)$$

Using 1 mm. of mercury as the unit of pressure, substitution of the numerical values of the constants for air gives the following equation for the mean constant-pressure expansion coefficient between  $0^\circ$  and  $100^\circ$  assuming  $\epsilon$  as the reciprocal of 273.135,

$$\epsilon_p = 0.00366119 + 12.45 \times 10^{-9} p_0 - 4.43 \times 10^{-14} p_0^2. \quad (4)$$

It is to be observed that the constant-pressure coefficient is a function of the temperature interval within which the expansion is measured since the coefficients of  $p_0$  and  $p_0^2$  in Equation 3 are a temperature function.

The formula for the constant volume coefficient is more simply obtained. Proceeding as before

$$\left[ \frac{\pi_1 - \pi_0}{\pi_0 t} \right]_v \quad (p_0 + \phi_0) t$$

Constant  $\omega$  is identical with constant volume and therefore  $\phi_1 = \phi_0$  at all temperatures is constant.  $\frac{p_1 - p_0}{p_0 t}$  is defined as  $\epsilon_v$  the constant volume coefficient of the actual gas and consequently

$$\epsilon_v = \epsilon + \epsilon \frac{\phi_0}{p_0} = \epsilon + \frac{A}{R^2 T_0^2} p_0. \quad (5)$$

The numerical values of the constants for air give the following equation where the pressure unit is mm.,

$$\epsilon_v = 0.00366119 + 12.93 \times 10^{-9} p_0. \quad (6)$$

It is to be noted that the pressure coefficient is independent of the temperature.

TABLE V.

THE VALUES OF THE EXPANSION COEFFICIENTS OF AIR CALCULATED IN THE ABOVE MANNER TOGETHER WITH THOSE MEASURED BY REGNAULT AND CHAPPUIS.

$p_0.$			$p_0.$		
$\epsilon_p \times 10^3.$			$\epsilon_p \times 10^3.$		
Mm.	Found.	Calc.	Mm.	Found.	Calc.
760	3.67060 (R)	3.67063	760	3.66500 (R)	3.67100
1000	3.67282 (C)	3.67360	1002	3.67440 (C)	3.67412
2525	3.69440 (R)	3.69230	2000	3.69030 (R)	3.68700
2620	3.69640 (R)	3.69380			

R = Regnault

C = Chappuis

### The Absolute Ice-Point Temperature.

The thermodynamic equation for the Joule-Thomson effect may be written as follows,

$$\mu c_p = T^2 \frac{\partial \frac{v}{T}}{\partial T}. \quad (7)$$

Integration of this equation leads to the equation of the constant pressure gas thermometer

$$\frac{v}{T} - \frac{v_o}{T_o} = c_p \int_{T_o}^T \frac{\mu}{T^2} dT = J_o^{100}. \quad (8)$$

The expansion coefficient  $\epsilon_p$  is defined through the equation  $v_{100} = v_o(1 + \epsilon_p 100)$  and for the fixed points  $0^\circ$  and  $100^\circ$ , Equation 8 may be re-arranged to give  $T_o$ , the absolute temperature of the ice point.

$$T_o = \frac{1}{\epsilon_p - \frac{T_{100}}{v_o 100} J_o^{100}}.$$

The integration of the Joule-Thomson effect member may be made by using the value of  $\mu$  formed from the equation of state and is as follows.

$$c_p \int_0^{100} \frac{\mu}{T^2} dT = \frac{2A}{R} \int_0^{100} \frac{dT}{T^3} - \beta \int_0^{100} \frac{dT}{T^2} = 1.963 \times 10^{-3}.$$

The ice-point temperature becomes then where the pressure is in mm.,

$$T_o = \frac{1}{\epsilon_p - 12.46 \times 10^{-3} \beta}.$$

Using the values of the expansion coefficients at constant pressure given in Table V gives the values of  $T_o$  appearing in Table VI.

TABLE VI.

$p_o$ . mm.	$\epsilon_p \times 10^3$ .	$\epsilon_p$ .	$\frac{1}{\epsilon_p}$ .	$T_o$ .	$\mu$ values used.
760	3.67060	Regnault	272.435	273.139	Calc.
1000	3.67282	Chappuis	272.270	273.197	Calc.
1000	3.67282	Chappuis	272.270	273.36	Hoxton
1000	3.67360	Calc.	272.212	273.305	Hoxton
2525	3.69440	Regnault	270.681	273.021	Calc.
					{Joule and Thomson
1000	3.67282	Chappuis	272.270	273.273	{Buckingham
1000	3.67360	Calc.	272.212	273.215	Buckingham
760	3.67063	Calc.	272.431	273.135	Calc.

It is evident that Regnault's value at 760 mm. and Chappuis' at 1000 mm. for the expansion coefficient are different when reduced to the same



pressure, by about 1 part in 4500, but also that the value of  $T_0$  from Regnault's coefficient (760 mm.) is more nearly in accord with the probable values of  $T_0$ , which latter is certainly not lower than 273.1 nor greater than 273.15. The 2525 mm. observation of Regnault is not sufficiently exact (1 part in 1700) for the present purpose for at such a pressure the distortion of the thermometer bulb by pressure becomes a serious factor.

The values of  $T_0$  derived from the measured values of  $\epsilon_p$  and  $\epsilon_v$  for nitrogen, hydrogen and helium have been given in a previous paper<sup>18</sup> and in the method of calculation employed, use was made of the pressure coefficients alone derived from the equation of state for the respective gases. In this method of computing  $T_0$  in no case does  $T_0$  come out greater than 273.153 while the most trustworthy expansion coefficients ( $\epsilon_v$ ) measured by Day and Clement, ranging in initial pressure from 314 mm. to 985 mm. give 273.133, 273.128, 273.147 and 273.139 or a mean value of 273.137. The expansion coefficients of the gases referred to lead to values of  $T_0$  which indicate therefore that Chappuis'  $\epsilon_p$  value of air at 1000 mm. is too small. The hydrogen  $\epsilon_v$  and  $\epsilon_p$  values of Chappuis, indeed, give by the same method of calculation  $T_0 = 273.147$ , and 273.115, respectively.

The conclusion appears inevitable, therefore, that the ice-point temperature as calculated from the Chappuis 1000 mm. value is too large because the latter value is too small by about one part in 4700 and the experimental values of  $\mu$  correlated as a function of the temperature to correct the  $\epsilon_p$  value are too large. The last horizontal entry in Table VI shows that the  $\mu$  equation derived from the equation of state gives with the calculated value of  $\epsilon_p$  an ice-point temperature (273.135) in accord with values of this constant obtained by other methods from the data on several gases.

If this value ( $T_0 = 273.135$ ) is accepted there is thus no escape from the conclusion that Chappuis' 1000 mm.  $\epsilon_p$  value for air is in error and at all events inconsistent with  $T_0$  deduced from his values obtained for other gases.

There is, however, still another method which may be used to obtain  $T_0$  which is independent of any equation of state. This consists simply of plotting the values of  $\epsilon_p$  and  $\epsilon_v$  with the corresponding pressures and finding where the most representative line cuts the  $\epsilon$  axis. Such a plot is given in Fig. 1 wherein there have been drawn the lines for  $\epsilon_p$  and  $\epsilon_v$  derived from the respective equations of state as a function of the pressure for the several gases; and the dimensions of the original chart are such that 1 mm. indicates 1 part in 90,000 for  $\epsilon$ . The most numerous and usable data are those for nitrogen; the series of Chappuis'  $\epsilon_v$  values are higher than those of Day and Clement, but, nevertheless, the representative line for Chappuis' data cuts the  $\epsilon$  axis at about  $3.66132 \times 10^{-3}$  giving

<sup>18</sup> THIS JOURNAL, 42, 54 (1920).

$T_0 = 273.126$ . The Day and Clement values are clearly represented by the line resulting from the equation of state, and accordingly  $T_0$  would be about 273.14. The constant-pressure values for nitrogen due to Eumorphopoulos obtained with the use of a quartz-bulb thermometer lead by extrapolation to  $T_0 = 273.147$ . The mean of all three values is close to 273.135. It will be noted in addition that the pressure coefficients

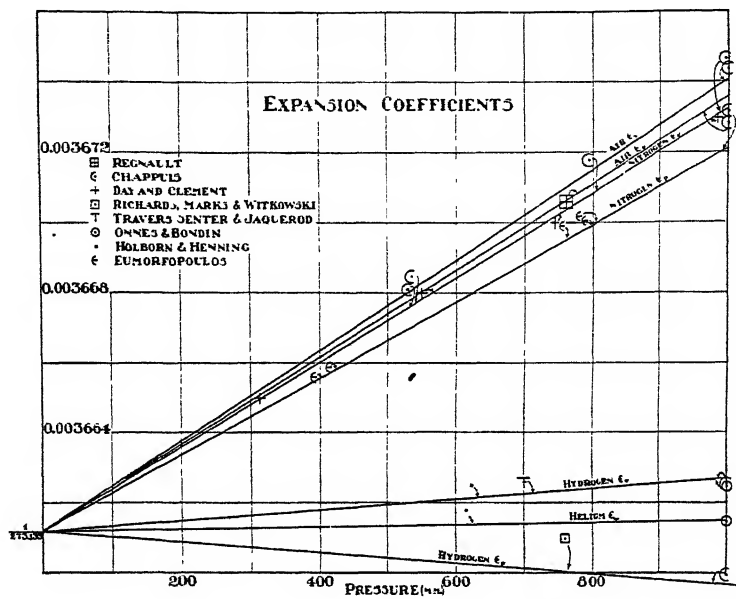


Fig. 1.

for  $\epsilon_p$  and  $\epsilon_p$  in the case of hydrogen are nearly equal numerically, but of opposite sign. The mean value of the two coefficients should be close to  $\frac{1}{T_0}$  and, in fact, amounts to  $3.366123 \times 10^{-3}$  whose reciprocal is 273.128.

Helium<sup>8</sup> is so nearly an ideal gas that almost any equation of state which approximately represents the isotherms should suffice. The equation which I have obtained based on the work of the Onnes laboratory leads to  $T_0 = 273.113$ . The mean of the graphically extrapolated  $\epsilon_p$  and  $\epsilon_p$  values then of Chappuis'  $\epsilon_p$  nitrogen values, Eumorphopoulos'  $\epsilon_p$  nitrogen values, Day and Clement's  $\epsilon_p$  nitrogen values is 273.137. Including the single helium  $\epsilon_p$  value of Holborn and Henning, the mean  $T_0$  amounts to 273.131.

It appears clear that  $T_0$  must be taken as very nearly 273.13 and the probability is that it does not exceed 273.14 in value, while Berthelot's value, 273.09, is judged therefore to be too low. With  $T_0$  assured, the conclusion is inevitable that all the measured Joule-Thomson numbers

are too large. A study of the original Joule-Thomson papers and all of the later communications offers no certain clue as to the probable reason for obtaining too large numbers, but if heat leaks or radiation effects of all kinds as well as "velocity cooling" disturbances may be assumed disposed of, there remain only two conceivable methods of changing the temperature of an isolated quantity of gas, in the sense that the internal energy change shall be equal to the energy element either  $p dv$  or  $d(pv)$ . In the former case, the temperature change produced per atmosphere at one atmosphere is about  $70^\circ$ , whereas in the latter it does not much exceed  $0.25^\circ$ .

The fine pores of the plug offer a resistance to the passage of the gas such as to maintain the pressure difference and it issues from the low-pressure face of the plug in fine streams of high velocity which presumably persist momentarily. There could be, therefore, local differences in density which result in further expansion against the gas on the low pressure side. It is in this region that a lower temperature results and only at a considerable distance from the plug would density and temperature differences be inappreciable. Unfortunately there is great difficulty in avoiding other sources of error such as heat conductance or radiation at a distance from the plug. It was noticed that the pressure coefficient observed by Hoxton is larger and this is the trend the measurements would take since the temperature change for the fine stream-persistence

suggested above is given by the equation  $\frac{dT}{dp} = T \frac{\left(\frac{\partial \eta}{\partial T}\right)_2}{C_p} \equiv \frac{RT}{p} \cdot \frac{1}{C_p}$  when  $p\eta = RT$ .

That is to say the effect of finite density differences expressed as a temperature change of this kind would be less at higher pressures. Thus there would result an apparent pressure coefficient much too large; furthermore, Joule-Thomson measurements made with high pressure differences would be more reliable than those with small pressure differences as is evident in the work of Bradley and Hale.

It is difficult to infer much from the work of Joule and Thomson on other gases than air, since in no case were the gases sufficiently pure to warrant great confidence in the numbers obtained. It is true in the case of nitrogen, oxygen, hydrogen and carbon dioxide, the attempt was made to correct for the impurities, but the relation between the Joule-Thomson effect in a given mixture and the Joule-Thomson effects in the constituents was then, as now, entirely unknown.

An examination of all the Joule-Thomson data available shows that the effect as related to temperature can be adequately represented within the limits of experimental error as a linear function of the inverse abso-

lute temperature as indicated in Fig. 2. This is clearly brought out by comparing the data plotted to different powers of the reciprocal absolute temperature. If the temperature function is linear in the reciprocal absolute temperature, there are no corrections required for the constant volume temperature scale,<sup>19</sup> supporting the form of the equation of state which adequately represents the pressures observed over such a wide range of both pressure and temperature. In any event, a very accurate means of establishing the linearity of the pressure increase with temperature at constant volume does lie in obtaining accurate measurements of the Joule-Thomson coefficients at various temperatures and low pressures (1 to 5 atmospheres) although the experimental difficulties are considerable.

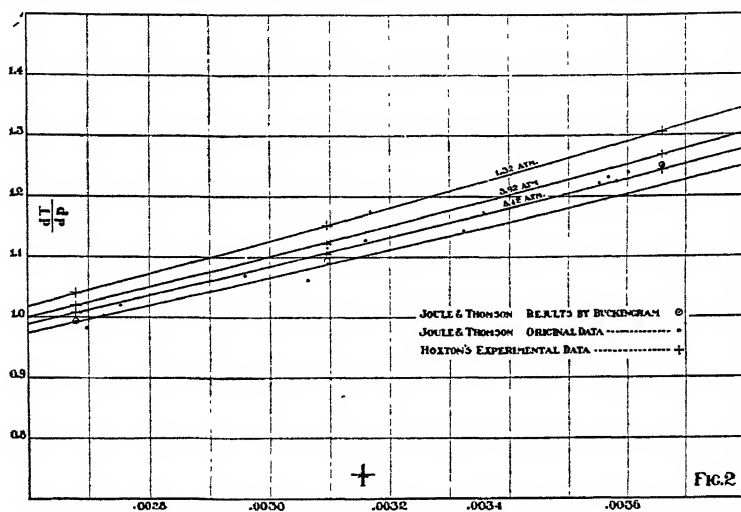


Fig. 2.

There is, however, one other method of attack bearing on the temperature function of the Joule-Thomson coefficient which consists of measuring the constant-volume specific heat at increasing pressures. Joly's data for air appear to indicate an increase of  $C_v$  with pressure, but an examination of his data for this gas leaves one entirely unconvinced regarding the dependence of the constant-volume specific heat on pressure. It becomes, in fact, a conviction that  $C_v$  is indeed constant from the data given when correction is made for the change in heat capacity of the copper sphere used due to the tension in the copper caused by the pressure of air within, for the compensating sphere on the opposite scale pan was exhausted. An attempt to make this correction follows.

<sup>19</sup> The calculated corrections for the constant-pressure scale from the equation of state for air follow easily from Equation 2 and accord well with the nitrogen scale corrections although several thousandths of a degree smaller than those calculated by Hoxton.

### The Joly Constant-Volume Specific-Heat Values for Air.

Joly presents seven measurements in the case of air at pressures varying from about 7 atmospheres to about 27 atmospheres. The copper spheres weighed 92.4 gr. and had a capacity of 159.8 cc. at  $15^{\circ}$ . There was, therefore, in each sphere 10.36 cc. of copper and the internal and external radii were respectively 3.3660 and 3.4373 cm. with a wall thickness of 0.0713 cm. Considering a patch on the surface of the sphere, it is perceived to be stretched under the internal pressure in two dimensions while the stresses along the radius will be neglected. Considering the thickness moreover as insignificant in comparison with the radius the tension on the copper section of a great circle due to the pressure of one atmosphere on a great area will be 24 atmospheres per cc. of copper. Consider then that each cubic centimeter of the copper has applied to its 4 faces intersected by a plane a uniform pull outward of 24 atmospheres for each atmosphere of gaseous pressure within the actual copper sphere. Assume further that a uniform pull of  $\frac{2}{3} \times 24 = 16$  atmospheres uniform tension on each face of the cubic centimeter will represent with sufficient approximation the actual state of tension in the copper sphere.

The change of specific heat with pressure is given by the equation,

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_p.$$

This equation is to be applied to the case of a tension in the material and  $\left(\frac{\partial^2 v}{\partial T^2}\right)_p$  assumed constant. Designating the specific heat of copper at zero tension as  $C_{p0}$  there is obtained for the difference of the specific heats at any tension  $p$ ,

$$C_p - C_{p0} = \left(\frac{\partial^2 v}{\partial T^2}\right)_p p.$$

Since the compensating sphere was exhausted it is unnecessary to subtract 1 from  $p$  to take account of the fact that the surrounding pressure was that of the atmosphere.

From Henning's recent work on the expansion of copper from  $-191^{\circ}$  to  $500^{\circ}$  the following equation was formulated giving the true expansion at every temperature  $T$ ,

$$\frac{1}{v_0} \frac{\partial v}{\partial T} = 31.94 \times 10^{-6} + 6.347 \times 10^{-8} T - 3.7 \times 10^{-11} T^2, \text{ and}$$

$$\frac{1}{v_0} \frac{\partial^2 v}{\partial T^2} = 6.35 \times 10^{-8} - 7.4 \times 10^{-11} T.$$

The numerical equation for the difference of the specific heats becomes for the 10.36 cc. of copper composing the sphere in calories per degree per atmosphere tension

$$C_p - C_{p0} = 5.07 \times 10^{-5} p$$

Joly's equation of the specific heat of air at constant volume is given as  $C_v = 0.17151 + 0.02788 \times \text{density}$ . The same equation in which the pressure is the variable instead of the density is  $C_v = 0.17151 + 3.3 \times 10^{-5} p$ . The coefficient of the increase of the specific heat of the copper sphere used to contain the gas is as has been shown to be  $5.07 \times 10^{-5}$  a number which is of the order of magnitude of Joly's coefficient  $3.3 \times 10^{-5}$ .

The actual experimental values are given in the order of pressure increase in the first column of Table VII. The third column gives the

TABLE VII.

The Joly Constant-Volume Specific Heat of Air.

Cv Air measured.	Pressure Atm.	Tension Sp. Heat corr.	Cv Air corrected.	Deviation from mean.
0.17202	6.81	0.00035	0.17169	+0.00048
0.17111	9.56	0.00049	0.17062	-0.00059
0.17193	13.56	0.00069	0.17124	+0.00003
0.17192	14.53	0.00074	0.17118	-0.00003
0.17252	14.58	0.00074	0.17178	+0.00057
0.17223	23.35	0.00119	0.17104	-0.00017
0.17225	26.62	0.00135	0.17090	-0.00031

Mean value 0.17121

correction corresponding to the pressure given in the second column as calculated by means of the specific-heat difference equation above for the copper sphere, while the fourth column contains the final specific-heat values whose mean is 0.1712. The last column contains the deviations from the mean value 0.1712. It is evident that the constant-volume specific heat of air is independent of pressure over the range of about 27 atmospheres at least.

The equation for the change of the constant-volume specific heat with volume is

$$\left( \frac{\partial C_v}{\partial v} \right)_T = T \left( \frac{\partial^2 p}{\partial T^2} \right)_v.$$

The left hand member is zero as shown by the measurements of Joly and hence  $\left( \frac{\partial^2 p}{\partial T^2} \right)_v = 0$  or  $\left( \frac{\partial p}{\partial T} \right)_v = \text{const.}$  which when integrated again gives  $[p]_v = \text{const.} \times T + \text{another constant.}$  The pressure is therefore a linear function of the temperature and at low pressures the Joule-Thomson effect must vary with respect to temperature linearly with the

inverse of the absolute temperature. This is also, as stated above, the conclusion from the data on the volume, pressure and temperature of air as given by my equation. The experimental data, in fact, of the Joule-Thomson effect at not too high pressures are represented by an equation of the form  $\mu = \frac{a}{T} - b$  as is indicated by Fig. 2.

The Joly data indicating independence of pressure of the constant-volume specific heat indicate also of course that the constant-volume air thermometer reads directly on the absolute scale and requires no correction. While explicit experimental confirmation is not as complete in the case of nitrogen, upon which our temperature scale rests, the same statement applies.<sup>18</sup>

### Summary.

1. The Joule-Thomson coefficients of air have been calculated from my equation of state for air based on the measurements of pressure, volume and temperature by Amagat, and have been compared with the coefficients as measured by Joule and Thomson, Noell and Hoxton. The measurements of Joule and Thomson accord well with the calculations except at zero degrees, while the recent careful measurements of Hoxton exceed the calculated values between 0 and 100° by about 15%.

2. The value of the ice-point absolute temperature (273.36) deduced from the Chappuis 1000 mm. constant-pressure expansion coefficient for air corrected by means of the Hoxton Joule-Thomson coefficients is too large, due to the fact that the Chappuis expansion coefficient is too small and the Joule-Thomson values too large. The calculated expansion coefficient and the Hoxton Joule-Thomson coefficients lead to  $T_0 = 273.197$ . The value  $T_0 = 273.135$  is on the other hand shown to be substantially correct in that this value is the mean value obtained by graphically extrapolating the measured constant volume and constant-pressure expansion coefficients of air, nitrogen, hydrogen and helium measured at various ice-point pressures. The value 273.135 is also the mean of  $T_0$  as deduced from the same data by means of the equations of state for the respective gases.

3. The pressure coefficient at zero of the Joule-Thomson coefficient as obtained by Hoxton is shown to be much larger than that obtained by other observers. The pressure coefficient given by Vogel and Noell ( $8.8 \times 10^{-4}$ ) is twice that calculated from the equation ( $4.5 \times 10^{-4}$ ) for low pressures, but agrees approximately with that calculated for high pressures, by means of the equation of state. The Bradley and Hale average pressure coefficient to 200 atmospheres at 0° is shown to be  $7.3 \times 10^{-4}$  while the average value over this range computed by the equation of state

is  $7.1 \times 10^{-4}$ . The Joule-Thomson coefficient itself at 1 atmosphere as given by Vogel and Noell is  $0.277^\circ$  and from Bradley's work  $0.268^\circ$ . The equation gives  $0.261^\circ$ .

4. An explanation of the discrepancies in the observed Joule-Thomson numbers is suggested which assumes that at the low-pressure surface of the plug a temperature drop is superposed on the Joule-Thomson temperature change due to the momentary persistence of the fine gas streams issuing from the pores of the plug and their subsequent expansion. It is shown that this effect would produce a large apparent pressure coefficient since the specific effect of the velocity-persistence-effect is shown to vary inversely as the pressure. The value of the measured Joule-Thomson effect at  $0^\circ$  and one atmosphere pressure is given as 0.303 by Hoxton, while that deduced from the high-pressure measurements of Bradley and Hale is 0.268, as compared with 0.261 calculated by the equation of state.

5. The Joly constant-volume specific heats of air are considered, and it is shown that a correction is required to compensate for the increased specific heat of the copper sphere used by Joly to contain the air. The corrected Joly values are shown to be independent of pressure, which fact confirms the validity of the form of the air equation of state employed. As a further consequence, it is pointed out that at low pressures the Joule-Thomson effect must vary inversely with the absolute temperature. Another important consequence is that the constant-volume air-thermometer scale reads directly on the absolute scale and therefore requires no correction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 363.]

## COMPOUND FORMATION AND SOLUBILITY IN SYSTEMS OF THE TYPE, FORMIC ACID:METAL FORMATE.

BY JAMES KENDALL AND HOWARD ADLER.

Received February 25, 1921.

The experimental work presented in the following pages has been carried out with the object of determining how far the conclusions arrived at in a similar study of systems of the type sulfuric acid: metal sulfate<sup>1</sup> may be considered as generally valid for systems  $HX : RX$ . In order to make the test as rigorous as possible, a careful selection of an acid diverse in all properties from sulfuric acid was necessary. Formic acid was finally chosen as a typical weak monobasic organic acid, contrasting strikingly with sulfuric acid, a typical strong dibasic inorganic acid. It

<sup>1</sup> Kendall and Landon, *THIS JOURNAL*, 42, 2131 (1920); Kendall and Davidson, *ibid.*, 43, 979 (1921).



is true that a still weaker acid might have been selected to obtain a more extreme contrast, but when it is noted that previous investigations on systems of the type  $\text{ROH} : \text{HOH}$  already furnish us with considerable data for the case of an exceedingly weak acid, the desirability of choosing an example of an intermediate type (such as formic acid) to complete the field becomes obvious. The instability of the formates of the more noble metals prevents a full survey of the series being made, but against this disadvantage is to be placed the convenience of the melting points of formic acid and its derivatives, which facilitates the experimental procedure and allows the various systems to be investigated through much larger concentration ranges than would otherwise be possible.<sup>2</sup> Furthermore, careful determinations of the conductivities of several formates in formic acid have been made by Schlesinger<sup>3</sup> and his co-workers, providing material for the future correlation of the results here obtained with ionization relationships, the final object of this work.<sup>4</sup> Nevertheless, in order that no gaps should be left in the series, a few systems of the type acetic-acid: metal-acetate have also been included in this investigation.

Practically no previous work of value has been done upon acid formates and acetates. Although Groschuff<sup>5</sup> employed the freezing-point method to examine certain of the formates with formic acid, the majority of the results obtained by him are considerably in error. A few acid acetates have been reported in isolated investigations, usually of great age and of doubtful accuracy, but no systematic study such as is here attempted has hitherto been undertaken.

In the present work the following systems have been examined: (a) with formic acid; potassium, ammonium, sodium, lithium, barium, calcium, magnesium, zinc, nickel, lead and copper formates: (b) with acetic acid; sodium, calcium, zinc, ferric and silver acetates.

in a modified Beckmann apparatus, the work at higher temperatures in sealed bulbs.

The more accurate freezing-point tube method could be employed only for temperatures below  $60^{\circ}$ , owing to the volatility of the acids at higher temperatures. In the sealed bulbs the air space was made as small as possible to reduce concentration changes in the solutions due to this cause. Fortunately, secondary disturbing factors such as were met with in the case of the sulfates<sup>7</sup> were here absent, so that the curves could be carried to much higher concentrations of salt than was there found feasible. A limit was set in most cases, however, by the decomposition temperature of the acid or of the neutral salt.<sup>8</sup> Only for potassium and ammonium formates, which are stable beyond their relatively low melting points, could the determinations be extended right through the complete system.

Formic acid was prepared from a standard C. P. product by treatment with boron trioxide for the removal of final traces of water.<sup>9</sup> Distillation *in vacuo* under anhydrous conditions was continued until a product melting at over  $8.4^{\circ}$  was obtained.<sup>10</sup> Acetic acid melting at  $16.5^{\circ}+$  was prepared by addition of acetic anhydride to glacial acid, as described by Kendall and Gross.<sup>11</sup> The preparation of the various metallic formates and acetates is given under their particular systems below.

Every possible precaution was taken to prevent entrance of moisture during determinations or contamination of materials with moisture before use. The extremely hygroscopic nature of certain of the salts restricted work on systems in which they formed one component to dry, cold days.

In some cases the compounds isolated were stable in the region of their melting points, and their compositions were consequently obtained immediately from the curves. When transition to another phase occurred

more interesting curves are also given in the accompanying diagrams. Compositions are expressed in molecular percentages throughout;  $T$  denotes the temperature of initial solidification.

### Results. (A) Formic Acid Systems.

**Potassium formate:Formic acid.**—The potassium salt was prepared by dissolving a pure sample of potassium carbonate in 90% formic acid. After all of the carbon dioxide had been expelled by heating, the hydrated salt was crystallized from the solution. This compound (which is exceedingly hygroscopic) was dried as completely as possible by prolonged heating just below its melting point; the last traces of moisture were removed by recrystallization from absolute ethyl alcohol and desiccation over 99% sulfuric acid *in vacuo*. The final product melted at  $167.5 \pm 0.5^\circ$ , which compares very favorably with the previously recorded value of Groschuff,<sup>12</sup>  $157^\circ$ .

#### (a) Solid phase H.COOK.

% H.COOK	0.0	0.97	3.02	4.73	6.36	8.43	10.74	12.63	13.88	15.57
$T$ .....	8.4	7.4	4.9	2.2	-0.9	-5.7	-12.6	-18.7	-23.8	-31.5

#### (b) Solid phase H. COOK, 3H.COOH (?).

% H.COOK.....	16.32	16.62	17.44	18.10	18.88
$T$ .....	-29.0	-27.3	-23.5	-21.7	-19.5

#### (c) Solid phase H.COOK, 2H.COOH.

% H.COOK.....	19.48	19.91	21.21	22.79
$T$ .....	-19.0	-16.0	-8.0	-0.6

#### (d) Solid phase H.COOK, H.COOH.

% H.COOK	23.04	24.14	25.98	28.56	30.41	31.97	33.74	37.29	38.34
$T$ ..	-10.1	7.3	29.9	53.0	65.1	72.9	80.6	93.0	96.1
% H.COOK	41.68	42.63	42.91	45.95	50.25	51.49	54.24	58.47	61.14
$T$ .....	103.2	104.3	104.6	107.5	108.6	108.2	107.2	103.4	100.6

#### (e) Solid phase H.COOK.

% H.COOK..	66.45	68.71	71.24	75.18	77.75	82.41	86.68	91.24	100.0
$T$ .....	108.1	114.5	122.3	130.7	135.8	143.6	150.0	157.3	167.5

The above results are reproduced graphically in Fig. 1. Three acid salts have been isolated, of which one (the equimolecular compound H.COOK, H.COOH) is stable right up to its melting point,  $108.6^\circ$ . This salt has been previously reported by Groschuff, but his statement that it undergoes transition before melting is obviously unjustified. The two remaining compounds have not been isolated before. Analysis of solid phase (c) gave an acid content of  $67.9 \pm 1.0$  mol. %, evidently corresponding to the compound H.COOK, 2H.COOH. Because of the low temperature ( $-17.5^\circ$ ) at which it undergoes transition, the composition of solid phase (b) could not be definitely determined. From the slope of the curve, however, the probable formula H.COOK, 3H.COOH is deduced.

**Ammonium Formate: Formic Acid.**—The ammonium salt was prepared by passing ammonia into 90% formic acid. Towards the end of the absorption, the temperature was raised sufficiently to ensure the deposition of the neutral (instead of the acid) salt. The product obtained was recrystallized from absolute alcohol and then desiccated over  $\text{P}_2\text{O}_5$ . The melting point of the final material was  $117.3 \pm 0.2^\circ$ .

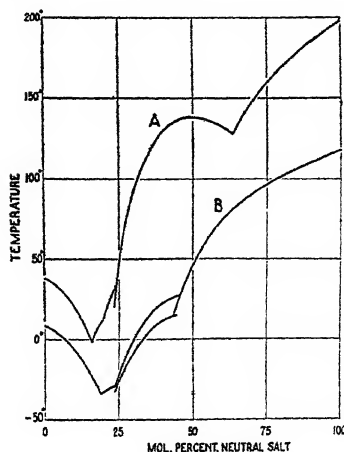


Fig. 1.—(A) Potassium formate:formic acid (subtract  $30^{\circ}$  from the temperature readings); (B) ammonium formate:formic acid.

(a) Solid phase  $\text{H.COOH}$ .

% $\text{H.COO.NH}_4$	0.0	1.53	3.70	6.28	8.19	10.14	12.43	14.86	17.11	18.95
T.....	8.47	7.0	4.5	0.6	-2.8	-6.9	-12.6	-19.8	-26.9	-33.8

(b) Solid phase  $\text{H.COO.NH}_4, 3\text{H.COOH}$ .

% $\text{H.COO.NH}_4$	20.43	21.73	23.33
T.....	-31.3	-30.0	-29.3

(c) Solid phase  $\text{H.COO.NH}_4, \text{H.COOH}$ .

% $\text{H.COO.NH}_4$ .....	23.33	24.83	25.41	26.64	27.90	30.11	33.25
T (unstable modification)	-32.5	-26.0	-23.5	-13.7	-14.0	...	1.3
T (stable modification)	....	....	....	-13.7	-8.7	0.7	10.4
% $\text{H.COO.NH}_4$	36.29	39.30	41.90	42.94	44.38	...	...
T (unstable modification)	7.4	11.3	13.8	14.3	15.0	...	...
T (stable modification)	17.3	22.2	24.9	25.8			

(d) Solid phase  $\text{H.COO.NH}_4$ .

% $\text{H.COO.NH}_4$	44.38	46.06	47.87	51.88	59.98	68.23	74.32	76.20
T.....	20.4	29.3	37.5	53.1	74.3	89.5	96.5	98.5
% $\text{H.COO.NH}_4$	83.46	88.41	91.64	100.0	...	...	...	...
T.....	103.7	108.5	111.7	117.3	...	...	...	...

Two distinct acidsalts are indicated, as will be seen from the diagram (Fig. 1). Both undergo transition before their melting points are reached, but in the case of solid phase (b) the curve so nearly reaches its maximum point before the salt becomes unstable that it is possible to assign to the compound the formula  $\text{H.COO.NH}_4, 3\text{H.COOH}$  and the approximate melting point of  $-29^{\circ}$ . The remaining compound exists in two different crystalline modifications, the stable form appearing from solution as needles, the unstable as prisms. Analyses of both forms gave the same acid content ( $49.4 \pm 0.6$  mol. % acid), indicating the equimolecular salt<sup>13</sup>  $\text{H.COO.NH}_4, \text{H.COOH}$ .

<sup>13</sup> This compound has been previously isolated in investigation by Reik (*Monats.*, 23, 1033).

**Sodium Formate:Formic Acid.**—The sodium salt was prepared from a reputed c. p. sample by two recrystallizations from water and desiccation at  $140^{\circ}$  to constant weight. The melting point obtained was  $255 \pm 1^{\circ}$ ; the value given by Groschuff is  $253^{\circ}$ .

(a) Solid phase  $\text{H.COONa}$ .

% $\text{H.COONa}$	0.0	1.04	2.92	4.61	6.35	8.72	10.50	12.58
$T$ .....	8.4	7.5	5.3	3.0	0.4	-3.8	-7.6	-12.8

(b) Solid phase  $\text{H.COONa}$ ,  $2\text{H.COOH}$ .

% $\text{H.COONa}$ ..	14.52	16.45	18.18	20.69	21.13	21.86	23.23	24.43	24.91
$T$ .....	-17.4	0.3	10.7	22.9	24.4	26.3	30.5	33.1	34.5

(c) Solid phase  $\text{H.COONa}$ ,  $\text{H.COOH}$ .

% $\text{H.COONa}$	25.18	25.90	27.00	27.10	28.39	29.80	31.15	31.65	32.14
$T$ .....	31.0	37.3	45.2	45.6	52.2	59.0	65.1	67.5	69.6

(d) Solid phase  $\text{H.COONa}$ .

% $\text{H.COONa}$	29.80	31.65	33.40	35.71	39.10	42.79	43.47
$T$ .....	45.1	63.6	81.2	99.3	118.6	135.2	137.7

Two acid salts are shown by the curves (see Fig. 2), both becoming unstable before their melting points are reached. Analyses of solid phase (b) gave an acid content of  $66.1 \pm 0.5$  mol. %, corresponding to the compound  $\text{H.COONa}$ ,  $2\text{H.COOH}$ . Analyses of solid phase (c) gave an acid content of  $50.1 \pm 0.2$  mol %, corresponding to the compound  $\text{H.COONa}$ ,  $\text{H.COOH}$ .

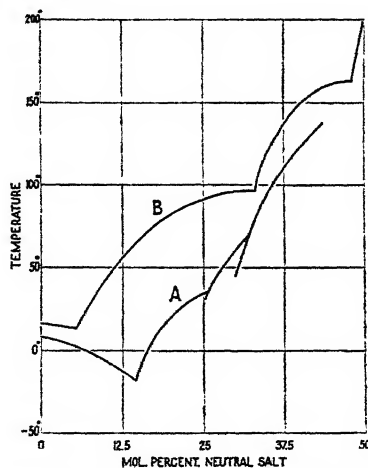


Fig. 2.—(A) Sodium formate:formic acid; (B) sodium acetate:acetic acid.

The curve could not be extended to the pure neutral salt, owing to the decomposition of the acid at temperatures above  $160^{\circ}$ . This places an automatic upper limit upon all other systems in which formic acid is one component.

It may be noted that the previous results of Groschuff upon this system are entirely in error.

**Lithium Formate:Formic Acid.**—Lithium formate was prepared from a pure sample of the carbonate and 90% formic acid. The hydrated salt which crystallized out from the solution was dehydrated at  $100^{\circ}$ , and final purification secured by recrystallization from alcohol and desiccation over sulfuric acid *in vacuo*.

(a) Solid phase  $\text{H.COOH}$ .

% $\text{H.COOLi}$	0.0	1.58	3.47	5.33	7.09	8.93	10.75	12.23	13.99
T.....	8.4	7.0	5.2	3.2	1.1	-1.3	-3.5	-5.6	-8.2
% $\text{H.COOLi}$	18.19	19.56	21.25	22.24	23.49	24.33	....	....	....
T.....	-14.6	-17.1	-19.8	-21.7	-23.5	-25.0	..	....	....

(b) Solid phase  $\text{H.COOLi}$ .

% $\text{H.COOLi}$	23.49	23.93	25.31	25.91	26.38	27.71	29.87	31.98
T.....	18.0	34.0	80.0	90.5	97.9	113.1	131.2	145.1
% $\text{H.COOLi}$	33.04	35.01	36.13	...	...	....	....	....
T.....	150.4	159.1	163.5	...	...	....	....	....

Contrary to expectations, no acid salts are indicated. The curve could not be carried to completion, but analyses of solid phase (b) showed it to be the neutral salt.

**Barium Formate:Formic Acid.**—The barium salt was obtained by the action of 90 % acid on the carbonate, as described above. It was recrystallized from water 3 times and dried to constant weight at  $140^\circ$ .

(a) Solid phase  $\text{H.COOH}$ .

% $(\text{H.COO})_2\text{Ba}$	0.0	0.91	1.74	2.30	3.73	4.67	5.12	6.95
T.....	8.4	7.2	6.1	5.1	2.6	0.5	-0.3	-4.9

(b) Solid phase  $(\text{H.COO})_2\text{Ba}$ ,  $\text{H.COOH}$ .

% $(\text{H.COO})_2\text{Ba}$	8.52	8.86	9.23	9.83	10.03	10.75
T.....	9.5	15.5	19.0	24.9	26.5	31.8

Owing to extreme retardation in the attainment of equilibrium<sup>14</sup> the system could not be investigated at concentrations greater than 10.7 mol % salt.<sup>15</sup> Analyses of solid phase (b) gave an acid content of  $50.6 \pm 0.7$  mol %, corresponding to the compound  $(\text{H.COO})_2\text{Ba}$ ,  $\text{H.COOH}$ . This salt has not been previously reported.

**Calcium Formate:Formic Acid.**—The method of preparation for calcium formate was the same as given for the barium salt.

(a) Solid phase  $\text{H.COOH}$ .

% $(\text{H.COO})_2\text{Ca}$	0.0	0.16	0.48	0.71	0.93	1.27	1.53
T.....	8.4	8.1	7.7	7.4	7.2	6.9	6.6

(b) Solid phase  $(\text{H.COO})_2\text{Ca}$ .

% $(\text{H.COO})_2\text{Ca}$	0.39	0.57	0.83	1.10	1.26	1.35	1.54	1.61
T.....	128.6	100.0	79.0	61.0	49.7	45.5	35.0	30.0

Analyses showed solid phase (b) to be the neutral salt. As will be seen from the curve (Fig. 3), this exhibits retrograde solubility in formic acid, the solubility at  $130^\circ$  being less than a quarter of that at  $30^\circ$ . It is interesting to find that a phenomenon which is so characteristic of calcium salts in aqueous solutions is here again evident.

**Magnesium Formate:Formic Acid.**—The salt was prepared by dissolving c. p. magnesia in 90 % acid, and dehydrating the product obtained (a dihydrate) to constant weight at  $110^\circ$ . Analysis showed that hydrolysis and consequent loss of acid during dehydration was negligible.

No curve could be obtained for this system owing to the insolubility of the salt in the pure acid. At  $25^\circ$  the saturated solution contains only 0.20 mol % of salt. At-

<sup>14</sup> Compare the system  $\text{BaSO}_4\text{:H}_2\text{SO}_4$ ; Kendall and Davidson, *loc. cit.*

<sup>15</sup> The last points determined represent metastable equilibria, since the solutions deposit, on long standing, crystals of a different form, probably the neutral salt. The solubility curve for this phase must be extremely steep, since a mixture containing 11 mol % of salt did not give a clear solution even at  $140^\circ$ .

tempts to obtain values at higher temperatures failed, equilibrium conditions in the sealed bulbs not being attainable.

**Zinc Formate:Formic Acid.**—The neutral salt was prepared from the carbonate. Its solubility in formic acid is practically zero, a mixture containing less than 0.16 mol % of salt not giving a clear solution even at 140°.

**Nickel Formate:Formic Acid.**—The hydrated salt was prepared from the carbonate and 90% acid, recrystallized from water, and dehydrated at 140°. The neutral salt obtained was soluble in formic acid to an extent of less than 0.10 mol % at 140°.

**Lead Formate:Formic Acid.**—The lead salt was prepared by precipitation from lead nitrate and sodium formate in aqueous solution. The precipitate was thoroughly washed, recrystallized twice from water and dried at 140°.

(a) Solid phase  $(\text{H.COO})_2\text{Pb}$ .

% $(\text{H.COO})_2\text{Pb}$	0.21	0.30	0.42	0.51
T.....	20.0	73.1	109.4	124.5

The solubility, while still extremely slight, is just measurable in this system. While the solid phase in equilibrium with the solutions could not be analyzed, the steepness of the curve leaves little doubt that it is the neutral salt.

**Copper Formate:Formic Acid.**—The hydrated salt was prepared from a pure sample of basic carbonate and 90% acid. After recrystallization from water it was dehydrated to constant weight at 80°, the bright blue neutral salt being obtained.<sup>15</sup> The solubility of this in pure formic acid is less than 0.10 mol % at 140°.

**Silver Formate:Formic Acid.**—Strenuous efforts were made to investigate this system, but the instability of the silver salt rendered all determinations useless. In the presence of water the salt decomposes extremely rapidly. It may be isolated by precipitation in absolute methyl alcohol, but the product so obtained decomposes during desiccation over sulfuric acid even though protected from the light.

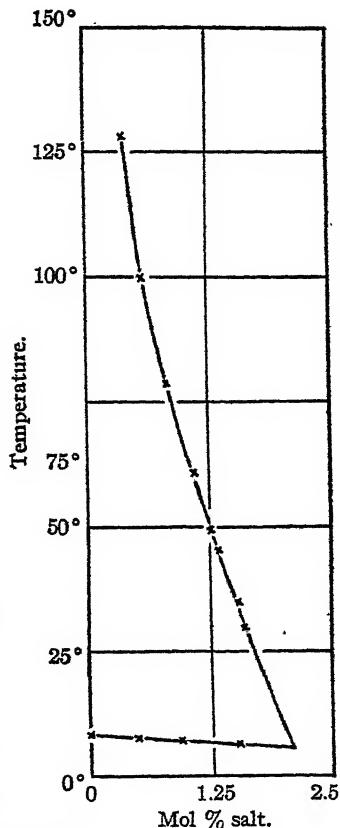


Fig. 3.—Calcium formate: formic acid.

## (B) Acetic Acid Systems.

**Sodium Acetate:Acetic Acid.**—The salt was prepared from a c. p. hydrate, which was recrystallized from water and dehydrated to constant weight at 140°. Analysis showed complete removal of water.

(a) Solid phase  $\text{CH}_3\text{COOH}$ .

% $\text{CH}_3\text{COONa}$	0.0	0.83	3.59	5.40
T.....	16.5	16.1	14.3	13.1

<sup>15</sup> Voss, *Ann.*, 266, 33 (1891).

(b) Solid phase  $\text{CH}_3\text{COONa}$ ,  $2\text{CH}_3\text{COOH}$ .

% $\text{CH}_3\text{COONa}$	7.11	8.92	12.17	15.27	16.58	21.55	26.86	30.72	33.03	33.16
T.....	25.3	36.7	54.3	66.9	71.9	85.7	93.2	96.1	96.25	96.3

(c) Solid phase  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$ .

% $\text{CH}_3\text{COONa}$	34.03	36.87	39.06	42.54	44.25	46.28
T.....	112.0	132.3	145.2	157.0	160.6	162.3

(d) Solid phase  $\text{CH}_3\text{COONa}$ .

% $\text{CH}_3\text{COONa}$	48.76	49.49
T.....	174.4	195.5

Two acid salts are indicated by the curves (see Fig. 2); both undergo transition just before reaching their maxima. By slight extrapolations on the diagram, however, the compositions of the compounds are obtained as  $\text{CH}_3\text{COONa}$ ,  $2\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$ , with melting points of  $96.3^\circ$  and  $164^\circ$  respectively. Both of these salts have been previously reported,<sup>17</sup> but the melting points given ( $80^\circ$  and  $140^\circ$ ) are considerably too low.

**Calcium Acetate:Acetic Acid.**—Anhydrous calcium acetate was found to be only slightly soluble in acetic acid. At  $30^\circ$  the saturated solution contains less than 0.35 mol % salt; no attempt was made to follow the curve to higher temperatures.

**Zinc Acetate:Acetic Acid.**—A c. p. sample of the salt was dehydrated at  $100^\circ$ . The anhydrous salt is practically insoluble in the pure acid, a mixture containing 0.10 mol % of salt giving a clear solution only at  $130^\circ$ .

**Ferric Acetate:Acetic Acid.**—A solution of ferric acetate in 90% acetic acid was treated with acetic anhydride and the mixture refluxed. The crystals deposited on cooling were dried with ether. Analysis showed the product obtained to be anhydrous and very slightly basic. The solubility in acetic acid was practically zero, a mixture containing only 0.07 mol % of salt not giving a clear solution even at  $140^\circ$ .

**Silver Acetate:Acetic Acid.**—The silver salt was prepared by precipitation from silver nitrate and sodium acetate. The precipitate was washed thoroughly, recrystallized from water and dried to constant weight over sulfuric acid *in vacuo*.

(a) Solid phase  $\text{CH}_3\text{COOAg}$ .

% $\text{CH}_3\text{COOAg}$	0.094	0.204
T.....	76.	115.

As will be seen, the solubility in acetic acid is very small. The measurements could not be carried to higher temperatures, owing to decomposition of the salt.

### Consideration of Results.

**Compounds isolated and their stability.**—The only formates that have been found to give isolable acid salts with formic acid are those of potassium, ammonium, sodium and barium. Of the 8 compounds obtained (one of which is existent in two crystalline modifications), only one is of sufficient stability to reach its melting point before undergoing transition. This is the equimolecular acid potassium salt, melting at  $108.6^\circ$ .

Obviously compound formation is here, as in the corresponding case of sulfates, most pronounced with the more electropositive metals, falling off rapidly as the electrode potential of the metal approaches that of hydrogen.

<sup>17</sup> Lescoeur, *Ann. chim. phys.*, [6] 28, 241 (1893). Vasiliev (*J. Russ. Phys. Chem. Soc.*, 41, 753 (1909)) has also studied the cryohydric point of this system.



The acid formates of potassium are more stable than those of sodium,<sup>18</sup> barium formate gives a single acid salt, while calcium and magnesium formates show no isolable compounds. Owing to the instability of silver formate, the increase in compound formation for metals below hydrogen in the electromotive series, so well illustrated in the case of the sulfates, is not here observable.

With acetates in acetic acid, although the full series has not been examined, the same behavior is evident. Sodium acetate gives 2 acid salts, both of which decompose just before reaching their melting points. Compounds of potassium,<sup>19</sup> ammonium<sup>20</sup> and lithium<sup>21</sup> acetates with acetic acid have been reported by previous investigators. The acetates of the less electropositive metals are practically insoluble in acetic acid.

It is of importance to note that the rate at which compound formation decreases in stability, as we go down the series from potassium to hydrogen, increases as the acid radical becomes weaker. Thus isolable acid sulfates are obtained even with zinc and ferrous iron, but the last isolable acid formate is reached as high up as barium. In general, therefore, the stability of the acid salts of any particular metal increases with the strength of the acid radical. Thus silver sulfate gives two acid salts with sulfuric acid, while silver acetate in acetic acid is scarcely soluble. Sufficient scattered observations may be collected from the literature to test this generalization for two other acid radicals. Acid *fluorides* have been reported for lithium,<sup>22</sup> potassium,<sup>23</sup> sodium,<sup>24</sup> ammonium<sup>25</sup> and silver.<sup>26</sup> With the last-named metal, 2 compounds (AgF, 3HF and AgF, HF) have been isolated; evidently compound formation in this series approaches in stability that given by the sulfates. With the much weaker *hydroxyl* radical, on the other hand, no tendency towards the formation of complexes is exhibited except with the highly electropositive metals. The only hydroxides which give isolable hydrates are those of the alkali metals,<sup>27</sup> ammonium,<sup>28</sup> barium<sup>29</sup> and strontium.<sup>30</sup>

<sup>18</sup> Lithium, the most electropositive metal of all, is out of line in giving a negative result; this, however, is a point which will be taken up later.

<sup>19</sup> Lescoeur, *Ann. chim. phys.*, [6] 28, 245 (1893); Melsens, *Compt. rend.*, 19, 611 (1844).

<sup>20</sup> Reik, *Monats.* 23, 1033 (1902).

<sup>21</sup> Lescoeur, *Bull. soc. chim.*, 24, 517 (1875).

<sup>22</sup> Abegg, *Handbuch der anorg. Chem.*, [1] 2, 120 (1908).

<sup>23</sup> Moissan, *Compt. rend.*, 106, 547 (1888).

<sup>24</sup> Abegg, *op. cit.*, p. 220.

<sup>25</sup> Marignac, *Ann. min.*, [5] 15, 221 (1859).

<sup>26</sup> Gore, *Proc. Roy. Soc.*, 18, 157 (1870); Guntz, *Bull. soc. chim.*, [3] 13, 114 (1895).

<sup>27</sup> Pickering, *J. Chem. Soc.*, 63, 890 (1893).

<sup>28</sup> Rupert, *THIS JOURNAL*, 31, 866 (1909); 32, 148 (1910).

<sup>29</sup> Abegg, *op. cit.*, [2] 2, 259 (1905).

<sup>30</sup> Müller-Erzbach, *Ber.*, 20, 1628 (1887); 22, 3180 (1889).

**Solubility Relationships.**—The parallelism between compound formation and solubility discovered in the case of the sulfates is again obvious in this work. The alkali formates are exceedingly soluble in formic acid, the salts of less electropositive metals are decreasingly soluble, practically zero solubility is shown by the formates of metals below magnesium in the electromotive series. The following table<sup>31</sup> exhibits the quantitative results at a single fixed temperature (25°).

Metal.	Electrode potential.	Mol % solubility 25°.	Solid phase.
Li	—3.02	23.7	H.COOLi
K	—2.92	25.5	H.COOK, H.COOH
Ba	—2.8 (?)	9.8	(H.COO) <sub>2</sub> Ba, H.COOH
Na	—2.72	21.3	H.COONa, 2H.COOH
Ca	—2.5 (?)	1.7	(H.COO) <sub>2</sub> Ca
Mg	—1.55	0.2	(H.COO) <sub>2</sub> Mg
Zn	—0.76	<0.1	(H.COO) <sub>2</sub> Zn
Ni	—0.22	<0.1	(H.COO) <sub>2</sub> Ni
Pb	—0.13	0.2	(H.COO) <sub>2</sub> Pb
Cu	+0.35	<0.1	(H.COO) <sub>2</sub> Cu

In the acetic acid series, solubilities follow the same course, as far as can be judged from the limited results available. Sodium acetate is very soluble in acetic acid, calcium acetate only slightly soluble, the acetates of less electropositive metals practically insoluble.

### Summary.

An examination of the freezing-point curves of metal formates in formic acid has resulted in the isolation of the following compounds.

Salt.	Acid compounds isolated.
Potassium formate	(a) H.COOK, 3H.COOH } (not previously reported)
	(b) H.COOK, 2H.COOH }
	(c) H.COOK, H.COOH; m. p. 108.6°
Ammonium formate	(a) H.COONH <sub>4</sub> , 3H.COOH (not previously reported)
	(b) H.COONH <sub>4</sub> , H.COOH; existent in 2 crystalline modifications
Sodium formate	(a) H.COONa, 2H.COOH (not previously reported)
	(b) H.COONa, H.COOH
Barium formate	(H.COO) <sub>2</sub> Ba, H.COOH (not previously reported)

The neutral formates of lithium, calcium, magnesium, zinc, nickel, lead and copper gave no isolable acid salts.

A few corresponding curves for metal acetates in acetic acid have been determined. With sodium acetate 2 acid salts (CH<sub>3</sub>.COONa, 2CH<sub>3</sub>.COOH

<sup>31</sup> Compare Kendall and Davidson, *loc. cit.*, p. 989. The only marked irregularity in the present table consists in the superior solubility of sodium formate over that of barium. This will be discussed in connection with the "valence factor" in compound formation in a later paper.

and  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$ ) were isolated; calcium, zinc, ferric and silver acetates gave negative results.

The results of this work resemble those obtained with sulfate systems in following the general rule previously deduced, that compound formation increases in extent with increasing diversity in the character of the components, the significant variable in systems of this general type  $\text{HX}:\text{RX}$  being the position of R relative to H in the electromotive series. An examination of the data for sulfates, formates, acetates, fluorides and hydroxides shows that the rate of decrease in compound formation as we proceed from more positive radicals (such as potassium) or less positive radicals (such as silver) towards hydrogen increases, the weaker the acid radical.

Solubility and compound formation are again found to proceed in parallel throughout the series. Salts which show extensive compound formation (such as salts of the alkali metals) are also extremely soluble. As we pass down the electromotive series towards hydrogen, solubility rapidly diminishes and finally becomes inappreciable.

The correlation of solubility with compound formation and of compound formation with ionization in solutions of metal formates in formic acid will be further dealt with in subsequent communications, and additional rules connecting these properties in systems of the general type  $\text{HX}:\text{RX}$  will there be formulated.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY  
No. 364.]

## THE PREDICTION OF SOLUBILITY IN POLAR SOLUTIONS.

BY JAMES KENDALL, ARTHUR W. DAVIDSON AND HOWARD ADLER.

Received March 3, 1921.

If all solutions were ideal, the answer to most of our solubility problems could be very simply stated.<sup>1</sup> At any given temperature the solubility of a solid substance A in a series of different solvents B, C, D, etc. would be, when expressed in terms of mol fractions, a fixed quantity, independent of the particular solvent and immediately calculable from the heat of fusion of A, the temperature of fusion of A and the specific heats of A in the solid and liquid states. All liquids would be completely miscible under all conditions. The solubility of a gas in a liquid, expressed again in terms of mol fractions, would depend only upon the ratio of its partial pressure over the solution to its vapor pressure in the liquid state at the same temperature.<sup>2</sup>

<sup>1</sup> Roozeboom, "Heterogene Gleichgewichte," [1] 2, 273, et seq. (1904); Washburn, "Principles of Physical Chemistry," Chap. 14 (1915).

<sup>2</sup> Strictly speaking, this would be true only for a perfect gas. More accurately, solubility is proportional to fugacity instead of to vapor pressure.

Unfortunately, we meet ideal solutions in the laboratory scarcely more frequently than we do infinitely dilute solutions, so that the theory of ideal solutions alone is not much more useful to us in the quantitative prediction of solubilities than is the simple theory of van't Hoff in the quantitative prediction of osmotic pressures or allied relationships. Certainly, for example, the solubility of iodine<sup>3</sup> is not the same in a series of solvents such as water, ethyl alcohol, chloroform, carbon disulfide and bromine at the ordinary temperature, even if translated from the units usually employed into terms of mol fractions.

In order to make any further advances on the basis of our modern theory of ideal solutions we require, therefore, to investigate very carefully the various factors which induce non-ideality in solutions and the effect each of these factors has on solubility phenomena. Apparently so many different points<sup>4</sup> are involved that the complexity of the problem, when first realized, almost compels us to despair of ever reaching definite conclusions; yet on critical examination it becomes possible to disentangle to some extent fundamental from secondary factors, and, by concentrating attention exclusively upon the former, to obtain at least a preliminary outline of the more comprehensive theory of solutions of the future.

This narrowing down of the point of attack may, of course, be carried too far, but in such a case vital disagreements between predicted and experimental results soon appear, necessitating a re-examination of the field already covered and leading either to the modification or to the amplification of the generalizations involved. Thus the tendency of most investigators in the field of non-ideal solutions has been to attribute all divergences from the ideal-solution equations to effects which may be called purely chemical, *i. e.*, to changes in the molecular state of the components on admixture.<sup>5</sup> In a recent extremely valuable series of articles by Hildebrand and his associates, however, the primary importance of taking into consideration two entirely distinct factors of a more physical nature, internal pressure and polarity, has been indisputably established.<sup>6</sup> The conclusions of Hildebrand with respect to the solubilities of solids in liquids (that section of the field to which the present article is restricted) may be

<sup>3</sup> Seidell, "Solubilities of Inorganic and Organic Compounds," 1919, pp. 325-34; Hildebrand, *THIS JOURNAL*, 39, 2299 (1917).

<sup>4</sup> Roozeboom, *op. cit.*, pp. 287-314.

<sup>5</sup> Dolezalek, *Z. physik. Chem.*, 64, 727 (1908); 71, 191 (1910); 83, 40 (1913); for other references see Findlay, "Osmotic Pressure," 1919, p. 64, *et seq.* Dhar, *Z. Elektrochem.*, 20, 57 (1914); also Kendall and Booge, *THIS JOURNAL*, 38, 1730 (1916); Kendall, Booge and Andrews, *ibid.*, 39, 2308 (1917).

<sup>6</sup> Hildebrand, *ibid.*, 38, 1452 (1916); 39, 2297 (1917); 41, 1067 (1919); Hildebrand, Ellefsen and Beebe, *ibid.*, 39, 2301 (1917); Hildebrand and Jenks, *ibid.*, 42, 2180 (1920); Hildebrand and Buehrer, *ibid.*, 42, 2213 (1920). Electromagnetic environment as a factor in solubility has also been considered by Harkins (*ibid.*, 41, 970 (1919)).

summarized as follows: (1) the solubility of a non-polar substance in a non-polar liquid of equal internal pressure is that calculated on the basis of the ideal-solution theory; (2) where the internal pressures are unequal, the solubility is less, to an extent depending on the difference in internal pressures; (3) when one substance is polar and the other non-polar, the solubility is also less; (4) when both substances are polar (leading frequently to the formation of recognizable compounds) the solubility is usually greater than the calculated value.

Numerous examples are given by Hildebrand to illustrate the first three of these rules. The greater difficulties inherent in the study of solutions of the fourth type (polar substances in each other) have also been briefly indicated.<sup>7</sup>

It is with this fourth class of solutions, particularly with those cases in which the formation of addition compounds between the components has already been extensively studied, that the present investigation is concerned. In previous articles<sup>8</sup> general rules have been formulated connecting the extent of compound formation with the difference in character<sup>9</sup> of the components of the solution, and for two series of systems of the type  $HX - RX$  a parallelism between compound formation and solubility throughout each series has been traced.<sup>10</sup> The fundamental significance of this parallelism is here discussed and its extension to other series attempted.

Before proceeding to a theoretical examination of these solutions (which belong, as indicated above, to the most complex of the 4 divisions made by Hildebrand) it is necessary to determine how many of the disturbing factors may legitimately be neglected, since only through such a clearing of the field in advance is it possible at the present stage to simplify matters sufficiently to enable us to formulate and put to the test any generalizations whatever.

In the first place, for the particular cases here examined, the factor of internal pressure may—in spite of what has been said above—be temporarily left out of consideration. Hildebrand<sup>11</sup> himself admits that there is more justification in restricting the discussion to purely chemical factors in mixtures involving a polar liquid; and the components of the mixtures

<sup>7</sup> Hildebrand, *THIS JOURNAL*, 38, 1464-1470 (1916).

<sup>8</sup> See particularly Kendall and Davidson, *THIS JOURNAL*, 43, 979 (1921); Kendall and Adler, *ibid.*, 43, 1470 (1921).

<sup>9</sup> *I. e.*, differences in the positive or negative nature of the constituent groups. In the case of systems of the simple type  $HX - RX$  here studied, where the negative radical  $X$  is common to both components, the difference in character is dependent on the relative positions of  $R$  and  $H$  in the electromotive series.

<sup>10</sup> Kendall and Davidson, *loc. cit.*, p. 989; Kendall and Adler, *loc. cit.*, p. 1480.

<sup>11</sup> Hildebrand, *THIS JOURNAL*, 38, 1461 (1916); see also Eastman and Hildebrand *ibid.*, 36, 2029 (1914).

investigated in this article are *both* polar. In a later section,<sup>12</sup> indeed, it will be shown that it is extremely improbable that the main conclusions here drawn can be significantly affected through not taking into account the differences in internal pressure of our components. The polarity factor, owing to its inherent complexity, cannot be disposed of so readily, but by dissecting the general term "polar," as applied to a liquid, into its particular consequences<sup>13</sup>—increased internal pressure, abnormalities in surface tension and other physico-chemical relationships, increased molecular complexity both in the pure state (association) and in solution with other polar substances (addition compound formation), and an increased tendency towards ionization—we can examine the effect of each of these in turn and so establish its relative importance in inducing deviations from ideality in the special class of solutions under study.

The results obtained in earlier papers of this series<sup>14</sup> lead us to conclude that *compound formation* between the components is the dominating point to be considered. *Internal pressures* in any particular system may vary considerably with the composition, but it has already been indicated that this factor can be here omitted. The abnormalities in other physical properties do not need to be taken into account in this work. *Ionization* has been shown to be a consequence of compound formation, and to parallel it in extent throughout any given series. Any divergences from the ideal solution laws due to compound formation between the components will, therefore, be accentuated by the accompanying ionization, it is true. But it is not to be expected that ionization will change the order of deviations from the ideal curve predicted for a series of systems on the basis of compound formation alone. Rather it will make the "spread" of the different curves with respect both to the ideal and to each other still more pronounced. A detailed discussion of the last remaining factor—*association* of the components—unfortunately cannot be entered into at this point for space considerations. In the final consideration of results,<sup>15</sup> however, it will be shown that the effect of this factor also is here, in general, only of secondary consequence.

We are now in a position to attack the problem in a simpler form, by investigating first of all the influence of compound formation alone upon ideal solution and solubility relationships. Rules for this factor having once been established, we can later proceed more readily to the consideration of the remaining factors.

<sup>12</sup> Page 1498 of this article.

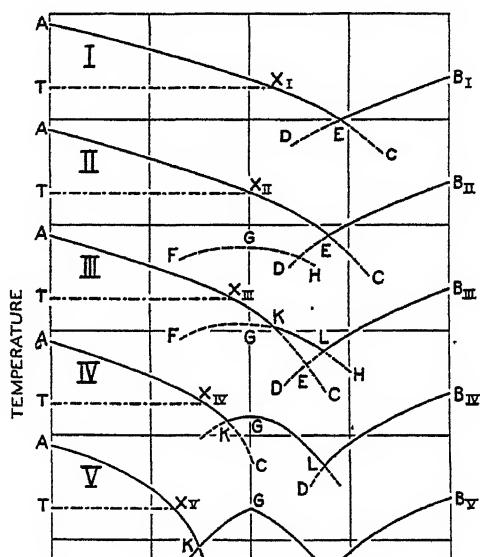
<sup>13</sup> G. N. Lewis, *THIS JOURNAL*, 38, 762 (1916).

<sup>14</sup> See especially Kendall and Gross, *ibid.*, 43, 1416, 1426 (1921).

<sup>15</sup> A preliminary treatment of this complicated subject is given by Roozeboom, "Heterogene Gleichgewichte," [1] 2, 303-14 (1904).

### The Effect of Compound Formation on the Ideal Solubility Curve.

The first stage of the problem consists in indicating qualitatively how the solubility of a fixed substance A will vary in a series of different solvents exhibiting gradually increasing compound formation with A in the liquid state. The complete solubility curves for such a series of systems are shown on a single diagram in Fig. 1. In this diagram, temperature is plotted against the molecular composition of the saturated solution. To facilitate comparison of the curves it is necessary to note that the point A represents the same temperature throughout—the melting point of pure substance A.



point of pure A, and  $R$  the gas constant 1.9852. The form and slope of this curve are conditioned solely by the ratio  $Q/T_0$ . If this ratio exceeds the value 4 (as it does for all substances except a few elements) the curve is concave throughout its whole course with respect to the composition axis, but does not change in slope greatly until  $x$  becomes very small, when it commences to dip sharply,  $x$  finally becoming zero at absolute zero of temperature. The solubility curve of  $B_I$  in A, the line  $B_ID$ , is similar in character (its slope depending, however, on the values of  $Q$  and  $T_0$  for  $B_I$ ). The stable portions of the two curves end at their point of intersection, E, the eutectic point of the system.

Curves II to V illustrate the successive changes which occur in the diagram as compound formation increases.<sup>18</sup> In Curve II the compound formed is so highly dissociated in solution that its solubility curve FGH never enters the stable region of the diagram; in Curve III compound formation is somewhat more extensive and the solubility curve of the compound  $AB_{III}$  possesses a limited stable interval KL; in Curve IV this interval has expanded sufficiently to exhibit a maximum point at G (in other words, the compound  $AB_{IV}$  is stable at its melting point); in Curve V, finally, the compound  $AB_V$  is not dissociated at all into its components in the solution, the system consisting, indeed, of two simple systems of the type shown in Curve I compressed into one composition range.

The essential point to be noted in these systems is the depression of the curve AC from its ideal position, which compound formation in solution necessitates.<sup>19</sup> If only part of the total A in solution exists as uncombined A then, since the solution will not become saturated with respect to A until the mol fraction of *uncombined* A reaches the ideal value, the mol fraction of A in the saturated solution must exceed



that we are approaching somewhat too closely systems of the type studied by Hildebrand (where internal pressure differences cannot be kept out of consideration), yet a uniform increase in solubility throughout each series is apparent.

TABLE I.<sup>a</sup>

Solubility at 40° of Dimethyl-pyrone  
(M. p., 132.1°).

Solvent.	Mol. % solute in saturated soln.
Acetic acid	40.2
Formic acid	46.8
Chloro-acetic acid	50.6
Dichloro-acetic acid	53.5
Trichloro-acetic acid	54.3
[Ideal (calc.) <sup>c</sup>	41.5]

<sup>a</sup> Kendall, THIS JOURNAL, 36, 1222 (1914).

<sup>b</sup> Kendall and Booge, *ibid.*, 38, 1712 (1916).

<sup>c</sup> Poma, *Gazz. chim. ital.*, [II] 41, 518 (1911). Approximate value only.

TABLE II.<sup>b</sup>

Solubility at 10° of Trichloro-acetic Acid  
(M. p., 58°).

Solvent.	Mol. % solute in saturated soln.
Benzene	38.0
Phenyl salicylate	57.5
Benzyl benzoate	64.4
Ethyl benzoate	66.0
Ethyl acetate	67.1

TABLE III.<sup>a</sup>

Solubility at 50° of Benzoic Acid  
(M. p., 121°).

Solvent.	Mol. % solute in saturated soln.
Benzene	17.6
Acetic acid	27.7
Chloro-acetic acid	

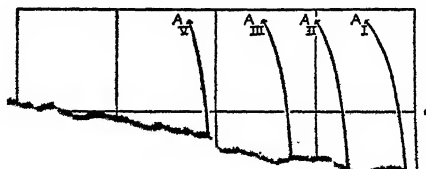
TABLE IV.<sup>b</sup>

Solubility at -5° of Ice  
(M. p., 0°).

Solvent.

### Solubilities of Different Substances in a Fixed Solvent.

This second stage of the problem (the comparison of the solubilities of a series of different solutes in the same solvent) is in practice the more important, owing to the supremacy of water as a solvent liquid. Theoretically, however, it is still more difficult to handle, for while the ideal solubility curve for each particular solute is fixed by its own values for  $Q$  and  $T_0$ , no relation between the values of either  $Q$  or  $T_0$  for *different* solutes has yet been established. We cannot therefore postulate in advance the relative positions of a series of ideal curves, much less make comparisons between them when compound formation causes deviations from the ideal. Under special circumstances, however, it is still possible to make some progress, namely when the solutes possess melting points far above the temperature at which we wish to conduct comparisons. The most interesting of all classes of solutes—neutral salts—fortunately falls under this category. For the discussion of solubility relationships in this field, reference should be made to Fig. 2.



in other words, the solubility is *practically zero*. If we take, as an example, the case of potassium chloride (for which  $Q$  is 64.10 cal. and  $T_0$  is  $1045^\circ$  abs.) we find that the mol fraction of the salt in a saturated ideal solution at  $25^\circ$  would be only 0.00044.<sup>23</sup>

If the salt forms a compound AB with the solvent, however, the solubility curve is depressed (as in Fig. 1) to an extent dependent upon the stability of the compound in solution, the successive changes which occur being shown in Curves II to V, as before.<sup>24</sup> The curve  $A_V C_V$ , which represents saturated solutions of a solute  $A_V$  forming a perfectly stable compound of the type AB, is tangential to the AB composition axis ( $x = 0.5$ ); the remaining curves again assume intermediate positions. Furthermore, since the curves are all falling exceedingly sharply in the lower portion of their courses, the variation of  $x$  with  $T$  at low temperatures is very small. It becomes a matter of minor importance, therefore, what the actual values of  $Q$  and  $T_0$  for each particular solute may be, since although the curves for the various salts intersect at random at high temperatures, at low temperatures the order of solubility will be substantially identical with the order of compound formation. As in Fig. 1 this may best be seen by comparing the positions of the points  $X_I$ ,  $X_{II}$ ,  $X_{III}$ ,  $X_{IV}$  and  $X_V$  on the various curves at a fixed temperature  $T$ . For strict purposes of comparison, it must be noted, it is essential that this temperature be so chosen that the solubility of the simple salt is determinable in each case. At still lower temperatures, where a compound may make its appearance as stable phase and the solubility of the simple salt may no longer be measurable, the solubility order may become obscured by the intersection of the stable curves, as indicated by the positions of the points  $X'_I$ ,  $X'_{II}$ ,  $X'_{III}$  and  $X'_V$  at the temperature  $T$ .<sup>1</sup> It must be emphasized that the solubility of the compound under such conditions affords no accurate guide to the actual solubility of the simple salt, but is useful in indicating its *minimum* value.<sup>25</sup>

For a series of different salts of high melting points in a fixed solvent at a sufficiently low temperature, therefore, solubility and compound formation again proceed in parallel. Two typical series which illustrate this rule (neutral sulfates in sulfuric acid and neutral formates in formic acid) have already been presented in previous articles, to which reference should be made for the complete tables. A third precisely similar series (metal hydroxides in water) may here be added for comparison.

<sup>23</sup> For a saturated aqueous solution, this is equivalent to about 1.8 g. per liter (approximately 0.02  $N$ ).

<sup>24</sup> Curve IV is omitted in order to avoid crowding and confusion in the diagram. Its position, however, between Curves III and V can readily be visualized with the aid of Fig. 1.

<sup>25</sup> The solubility of an unstable solid phase is necessarily greater than that of the stable solid phase.

TABLE V.

Solubilities of Metal Hydroxides in Water. 25°.				
Metal.	Electrode potential.	G. of hydroxide in 100 g. satd. soln.	Solid phase to which saturation refers.	Mol. % hydroxide in satd. soln.
Li	-3.02	11.14 <sup>a</sup>	LiOH, H <sub>2</sub> O	8.82
K	-2.92	54.2 <sup>a</sup>	KOH, 2H <sub>2</sub> O	29.13
Ba	-2.8 (?)	4.47 <sup>b</sup>	Ba(OH) <sub>2</sub> , 8H <sub>2</sub> O	0.489
Na	-2.72	53.2 <sup>a</sup>	NaOH, H <sub>2</sub> O	34.01
Sr	-2.7 (?)	1.016 <sup>c</sup>	Sr(OH) <sub>2</sub> , 8H <sub>2</sub> O	0.143
Ca	-2.5 (?)	0.152 <sup>d</sup>	Ca(OH) <sub>2</sub>	0.0370
Mg	-1.55	0.0012 <sup>a</sup>	Mg(OH) <sub>2</sub>	0.00052
Al	-1.34	insoluble	Al(OH) <sub>3</sub>	practically zero
Zn	-0.76	0.001 <sup>f</sup>	Zn(OH) <sub>2</sub>	0.00018
Cd	-0.40	0.00026 <sup>f</sup>	Cd(OH) <sub>2</sub>	0.000032
Ni	-0.22	insoluble	Ni(OH) <sub>2</sub>	practically zero
Pb	-0.13	0.0161 (?) <sup>g</sup>	Pb(OH) <sub>2</sub>	0.00121 (?)
Fe (ic)	-0.04	insoluble	Fe(OH) <sub>3</sub>	practically zero
Cu	+0.35	insoluble	Cu(OH) <sub>2</sub>	practically zero
Ag	+0.80	0.0054 <sup>h</sup>	Ag <sub>2</sub> O	0.00078

<sup>a</sup> Pickering, *J. Chem. Soc.*, 63, 890 (1893).

<sup>b</sup> Parsons and Corson, *THIS JOURNAL*, 32, 1383 (1910).

<sup>c</sup> Rothmund, *Z. physik. Chem.*, 69, 523 (1910).

<sup>d</sup> Bassett and Taylor, *J. Chem. Soc.*, 105, 1926 (1914).

<sup>e</sup> Tamm, *Z. physik. Chem.*, 74, 499 (1910).

<sup>f</sup> Bodländer, *ibid.*, 27, 66 (1898).

<sup>g</sup> Schnal, *Compt. rend.*, 148, 1394 (1909). In view of the results of earlier observers (see Seidell, "Solubilities of Inorganic and Organic Compounds," 1919, p. 362) this value must be regarded as somewhat uncertain.

<sup>h</sup> Rebière, *Bull. soc. chem.*, [IV] 17, 268 (1915).

The metals are arranged in the order of their electrode potentials. As in the two earlier series, it will be evident that the relative position of each metal to hydrogen in the series is the determining factor in compound formation, ionization and order of solubility. The hydroxides of those metals in the immediate neighborhood of hydrogen form no isolable hydrates, are practically non-ionized in solution and insoluble. As we proceed away from hydrogen towards the more electropositive metals we find isolable hydrates appearing and solubility increasing. The series culminates in the alkali hydroxides, which give a large number of very stable hydrates, are very highly ionized and are exceedingly soluble in water. The irregularities among the alkali metals themselves are to be ascribed to the fact that the solubilities of their non-hydrated hydroxides cannot be directly measured, the figures given being merely minimum values, as explained above.

As in the case of the formates, the available data for confirming an increase in hydration, ionization and solubility for metals below hydrogen are not very plentiful. Silver hydroxide is not stable in the solid state, so

that its solubility cannot be directly measured. It does exist in solution, however, as a moderately strong base,<sup>26</sup> and the solubility of this in water must be in excess of that of the more stable silver oxide.

The only marked exception, as before, is offered by aluminum; in spite of the high electrode potential of the metal, aluminum hydroxide is highly insoluble and is an exceedingly weak base. This abnormality<sup>27</sup> will be discussed later.

### Systems of the Type RX:HOH.

It is not possible to extend the general rules deduced for systems of the type RX:HX to other series of salts in water (where the system contains no radical common to both components) very far at present. The rules outlined above may be tentatively applied, however, to systems of the type RX:HOH for those particular series in which either R is not very different in character from H, or X is not very different in character from OH. In other words, we find that salts of a very weak base exhibit, in general, increasing hydrate formation and increasing solubility in water as the acid radical X diverges from OH, while salts of a very weak acid show the same behavior as the metal radical R diverges from H. Two illustrative series are presented below.

TABLE VI.

Solubility of Ferrous Salts in Water. 25°.

Salt.	Mol. % in satd. soln.	Stable solid phase.
FeCl <sub>2</sub>	8.97 <sup>a</sup>	FeCl <sub>2</sub> , 4H <sub>2</sub> O
FeBr <sub>2</sub>	8.99 <sup>a</sup>	FeBr <sub>2</sub> , 6H <sub>2</sub> O
Fe(NO <sub>3</sub> ) <sub>2</sub>	8.08 <sup>b</sup>	Fe(NO <sub>3</sub> ) <sub>2</sub> , 6H <sub>2</sub> O
FeSO <sub>4</sub>	3.39 <sup>c</sup>	FeSO <sub>4</sub> , 7H <sub>2</sub> O
FeC <sub>2</sub> O <sub>4</sub>	0.00097 <sup>d</sup>	FeC <sub>2</sub> O <sub>4</sub>
FeS	0.00013(?) <sup>e</sup>	FeS
Fe(OH) <sub>2</sub>	0.00013(?) <sup>f</sup>	Fe(OH) <sub>2</sub>

TABLE VII.

Solubility of Fluorides in Water. 18°.

Salt.	Mol. % in satd. soln.	Stable solid phase.
KF	14.79 <sup>g</sup>	KF, 4H <sub>2</sub> O
BaF <sub>2</sub>	0.0166 <sup>h</sup>	BaF <sub>2</sub>
NaF	1.85 <sup>i</sup>	NaF
SrF <sub>2</sub>	0.0017 <sup>k</sup>	SrF <sub>2</sub>
CaF <sub>2</sub>	0.00037 <sup>k</sup>	CaF <sub>2</sub>
.....	.....	.....
AgF	18.0(approx.) <sup>j</sup>	AgF, 4H <sub>2</sub> O

<sup>a</sup> Etard, *Ann. chim. phys.*, [7] 2, 537 (1894).<sup>b</sup> Funk, *Wiss. Abh. p. t. Reichsanstalt*, 3, 440 (1900).<sup>c</sup> Fraenkel, *Z. anorg. Chem.*, 55, 228 (1907).<sup>d</sup> Schaefer, *ibid.*, 45, 310 (1905).<sup>e</sup> Weigel, *Z. physik. Chem.*, 58, 294 (1907). Approximate value only.<sup>f</sup> Bineau, *Compt. rend.*, 41, 510 (1855). Approximate value only.<sup>g</sup> De Forcrand, *ibid.*, 152, 1210 (1911).<sup>h</sup> Kohlrausch, *Z. physik. Chem.*, 64, 145 (1900).<sup>i</sup> Mylius and Funk, *Ber.*, 30, 1718 (1897).<sup>j</sup> Guntz and Guntz, *Ann. chim.*, 2, 101 (1914). The solubility of the tetrahydrate is changing very rapidly with temperature at 18°, owing to the proximity of the maximum point.<sup>k</sup> Levi, *Gazz. chim. ital.*, [2] 31, 1 (1901).<sup>27</sup> See Kendall and Davidson, *THIS JOURNAL*, 43, 988 (1921); also Heyrovsky, *J. Chem. Soc.*, 117, 1024 (1920).

The results given above for ferrous salts are paralleled by the salts of other exceedingly weak bases (*e. g.*,  $\text{Zn}(\text{OH})_2$ ;  $\text{Cu}(\text{OH})_2$ ), the halides of these metals being all very soluble, the sulfates somewhat less so, and the carbonates, sulfides, etc. all practically insoluble. The strength of the base cannot be increased very far above that of water, however, before these rules become inapplicable. Thus, for example, lead sulfate is insoluble in water while lead acetate is very soluble.

The fluorides in Table VII form a very striking series. Solubility and compound formation both fall off rapidly as we go down the list from potassium to the less positive metals,<sup>28</sup> but with the silver salt the effect of the diversity factor again becomes very apparent. Similar solubility relationships hold, in general, for the salts of other weak acids, such as the carbonates, sulfides and cyanides.<sup>29</sup> In all these series, the salts of the alkali metals are very soluble in water, those of the alkali earth metals less soluble and those of the remaining metals practically insoluble. The rule noted in an earlier article<sup>30</sup> for systems of the type  $\text{HX}:\text{RX}$  when X is varied also applies here, namely that the decrease in solubility as we proceed towards hydrogen in the series is more rapid the weaker the acid radical X. The strength of this radical cannot be increased very far above that of water, however, before we find that all generalizations must be applied with considerable caution. It is somewhat surprising that they should still hold so well in the case of the fluorides.

For salts of a strong acid with a strong base, where we have simultaneously a positive radical very different in character from hydrogen and a negative radical very different in character from hydroxyl, no rules of a general nature can be deduced at present. It is true that Bodländer,<sup>31</sup> more than twenty years ago, made some extremely significant preliminary advances in this field by showing that the solubility of a difficultly soluble salt in water could be approximately calculated from the electrode potentials of its ions and the heat of formation of the solid salt, but the subsequent development of Bodländer's work has by no means equalled its early

<sup>28</sup> The order of barium and sodium is reversed, as in the case of the fluorides in hydrofluoric acid (Kendall and Adler, *loc. cit.*, p. 1479); this point however will be taken up later.

<sup>29</sup> Seidell, *op. cit.* It must be noted that the majority of the values given in the literature for these salts do not represent exact equilibrium data. For example, in the case of the carbonates, a definite solubility is obtained only when the partial pressure of  $\text{CO}_2$  above the solution is fixed (Johnston, *THIS JOURNAL*, 37, 2001 (1915)). Similarly a fixed  $\text{H}_2\text{S}$  pressure is necessary in the case of the sulfides, a point hitherto overlooked in the calculation of their solubilities. The current values (*e. g.*, those given by Weigel, *Z. physik. Chem.*, 58, 293 (1907)) may consequently not be legitimately comparable.

<sup>30</sup> Kendall and Adler, *loc. cit.*, p. 1479.

<sup>31</sup> Bodländer, *Z. physik. Chem.*, 27, 55 (1898).

promise,<sup>32</sup> and criticisms have been abundant.<sup>33</sup> Certain of these criticisms (such as the fact that the heat of formation of a compound is not an exact measure of the free energy change) were forestalled by Bodländer himself, but the really fundamental weakness in his method—the total neglect of the part played by the *solvent* in solubility phenomena—has not previously been sufficiently emphasized. It is due to this neglect that the rules formulated by Bodländer<sup>34</sup> regarding the relative solubilities of series of salts containing the same acidic or basic radical (rules which are substantially similar, for certain series, to those developed above) are restricted to aqueous solutions, and even there display disconcerting discrepancies.<sup>35</sup> Certainly the equilibria involved in aqueous salt solutions, owing to interaction between solvent and solute, are much more complicated than Bodländer assumed.<sup>36</sup> We can, however, by taking into consideration the effect of the formation of solvent-solute complexes on solubility relationships, not only carry the qualitative study of the question for the particular case of aqueous solutions to a point beyond that reached by Bodländer, but we can also apply the rules obtained to the more general field of non-aqueous solutions. A very brief survey of a few typical series is all that can be presented at this stage.

### The Solubility of Salts in Non-aqueous Solvents.

It has been claimed by Walden that the solubility of a salt in a series of solvents is greater the greater the degree of association (*i. e.*, the more marked the polar nature) of the solvent.<sup>37</sup> In the so-called "indifferent" solvents (such as hexane, benzene, ether) where compound formation is practically non-existent and where, furthermore, the difference in internal

<sup>32</sup> Abegg and Bodländer, *Z. anorg. Chem.*, **20**, 457 (1900); **34**, 180 (1903); *Am. Chem. J.*, **28**, 220 (1902).

<sup>33</sup> Ostwald, *Z. physik. Chem.*, **32**, 182 (1900); Locke, *Am. Chem. J.*, **27**, 105 (1902); **28**, 403 (1902); Noyes, *Z. physik. Chem.*, **42**, 507 (1903); Hildebrand, *THIS JOURNAL*, **38**, 1452 (1916). The following comment of Roozeboom upon the work of Bodländer is of particular interest: "To me it seems especially suspicious that temperature of fusion and heat of fusion have been left entirely out of consideration, since in ideal solutions these are the factors which absolutely control the solubility curve" (*Heterogene Gleichgewichte*, [1] **2**, 316 (1904)).

<sup>34</sup> Bodländer, *loc. cit.*, p. 69.

<sup>35</sup> Especially among *soluble* salts, where it was found necessary to add to the original theory a "law of self-preservation" to account for inverse solubility results (Abegg and Bodländer, *Am. Chem. J.*, **28**, 222 (1902)).

<sup>36</sup> Compare Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921); Kendall and Gross, *THIS JOURNAL*, **43**, 1425 (1921).

<sup>37</sup> Walden, *Z. physik. Chem.*, **55**, 703 (1906); **61**, 633 (1908). The rate of increase varies with the degree of association of the salt (see Turner, *J. Chem. Soc.*, **99**, 902 (1911)). An attempt to put Walden's rule upon a mathematical basis has been made by van Laar, *Z. physik. Chem.*, **58**, 567 (1907); **59**, 212 (1907).

pressure is extreme, salts are in general insoluble.<sup>38</sup> As the polarity of the solvent molecule increases, however, compound formation becomes more and more extensive and solubility increases. Where the compounds are sufficiently stable to be isolated from solution (as, for example, the acetic acid or alcohol addition products of calcium chloride) the solubility of the salt is very high.<sup>39</sup>

Walden's rule is only a partial statement of the facts, however. For a salt to be soluble it is not sufficient for the solvent molecule to be polar, its radicals must also be diverse in character from those of the solute. This has already been shown in detail for the 3 series of metal sulfates in sulfuric acid, metal formates in formic acid and metal hydroxides in water. Any salt  $RX$  in its own acid  $HX$ , indeed, necessarily possesses the characteristics of a base,<sup>40</sup> and the diversity of the radicals  $R$  and  $H$  will control compound formation and solubility. This rule may be further illustrated from the work of Franklin on liquid ammonia solutions.<sup>41</sup> Here the typical bases are the metal amides, imides and nitrides. Among those that are known only those of the alkali metals (*e. g.*, potassium amide, where the diversity between  $K$  and  $H$  is extreme) are soluble in ammonia. The ammonobases of the metals nearer to hydrogen (like the corresponding aquo-bases) are not soluble to any extent, and may be conveniently prepared by precipitation.

Aquo-acids and ammono-acids are similarly comparable. Although the majority of the common acids have melting points too low to enable us to discuss systems of the type  $HX:HOH$  in the same definite manner as systems of the type  $ROH:HOH$  in Table V, yet an analogous solubility rule, that strong acids, as a class, are much more soluble than weak acids, is obviously in general accordance with the experimental facts. In liquid ammonia the ammonium salts behave as acids, and here also we find that compound formation and solubility increase with the increasing strength of the acidic radical. Thus ammonium fluoride is insoluble, while the remaining ammonium halides are highly soluble and give very stable addition compounds.<sup>42</sup>

When we attempt to consider salts of other metals in liquid ammonia,<sup>43</sup> we encounter the same difficulties as for salts in aqueous solution. An interesting point<sup>44</sup> to notice, however, is that while hydrate formation and solubility in water are most extensive, in general, with salts of the most

<sup>38</sup> An interesting exception, silver perchlorate in benzene, has recently been critically investigated by Hill, *THIS JOURNAL*, 43, 254 (1921).

<sup>39</sup> Menshutkin, *Mem. Polyt. Inst. Petrograd*, 5, 355 (1906).

<sup>40</sup> Schlesinger and Calvert, *THIS JOURNAL*, 33, 1933 (1911).

<sup>41</sup> Franklin, *Am. Chem. J.*, 47, 285 (1912).

<sup>42</sup> Kendall and Davidson (J. G.), *THIS JOURNAL*, 42, 1141 (1920).

<sup>43</sup> Franklin and Kraus, *Am. Chem. J.*, 20, 820 (1898).

<sup>44</sup> Compare Hildebrand, *THIS JOURNAL*, 38, 1471 (1916).



electro-positive metals (*e. g.*, Li, K), the tendency to combine with and dissolve in ammonia is most marked for the salts of metals at the other extreme of the electrode potential series (*e. g.*, Hg, Ag). A possible explanation of this dissimilarity is the highly electropositive character of the ammonium group.<sup>45</sup>

Systematic solubility determinations for salts in other liquids are now in progress.

### The Solubilities of Salts in Aqueous Solutions of Other Salts.

So far, only two-component systems have been discussed. We can also gain information, however, regarding the general applicability of the rules here derived for systems of the type  $HX:RX$  to systems of the somewhat more general type  $RX:R'X$  (or  $RX:RY$ ) by examining the effect of the addition of a salt with a common ion upon the solubility of a difficultly soluble salt in water. As a typical illustration, the influence of other chlorides upon the solubility of silver chloride in water may be considered.

Normally, the solubility of silver chloride in water should be depressed practically to zero by the presence of another chloride in quantity, according to the principle of the constancy of the solubility product. If, however, any addition compounds between silver chloride and the added chloride  $MCl$  are formed in solution, then the solubility of silver chloride should exceed the calculated value by an amount dependent upon the stability of the compounds formed. The stability of the addition compounds, furthermore, should depend (according to the generalizations developed above) upon the diversity in the positions of the radicals Ag and M in the electrode potential series. Consequently we should expect the solubility of silver chloride in water to increase more and more above the normal value as the radical M is made more electropositive.

That this is so in actual fact is strikingly shown in Fig. 3, which reproduces the accurate determinations of Forbes.<sup>46</sup> It will be seen that the solubility is tremendously increased in every case shown, the order being  $H < Ca < Na < Sr < Ba < K$  or  $NH_4$ . This is exactly the order in the electrode potential series,<sup>47</sup> as may be seen by reference to Table V. In concentrated

<sup>45</sup> Although it has been shown by Frenzel (*Z. Elektrochem.*, 6, 486 (1900)) that the primary dissociation of ammonia is into  $H^+$  and  $NH_4^+$ , solvation of the positive ion to  $NH_4^+$  must also be admitted (compare Abegg, "Handbuch anorg. Chem.," [3] 3, 58 (1907)).

<sup>46</sup> Forbes, *THIS JOURNAL*, 33, 1937 (1911). The curves run very close together at low concentrations of added salt, consequently to avoid confusing the diagram the data for high concentrations only (above 2*N*) are there included. The solubility of  $AgCl$  in pure water at 25° is 0.0000120 g. equiv. per liter (Glowczynski, *Kolloidchem. Beihefte*, 6, 147 (1914)); practically zero on the scale in the diagram.

<sup>47</sup> The position of  $NH_4$  in the series, which cannot of course be directly determined, has been discussed thoroughly by Abegg ("Handbuch anorg. Chem.," [3] 3, 241-2

aqueous solutions of mercuric chloride, moreover, silver chloride is practically insoluble, as might also have been predicted from the proximity of Ag and Hg (ic) in the same table. For the influence of other chlorides upon the solubility of silver chloride in water no trustworthy data are at present available,<sup>48</sup> but experiments to complete the series are now being carried out in this laboratory.

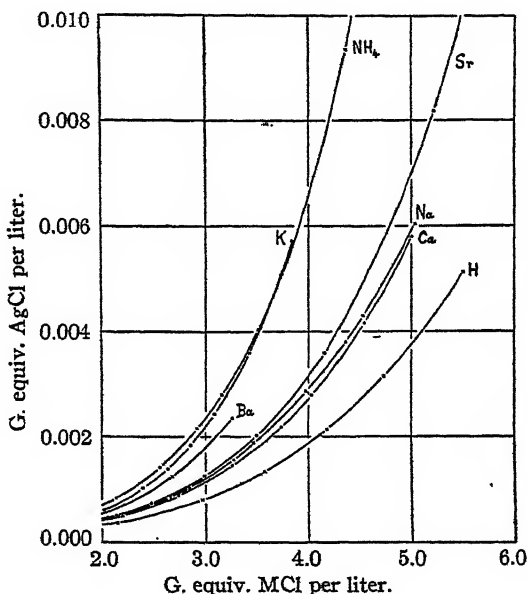


Fig. 3.

A very wide and promising field for future investigation here offers itself, since it will be obvious that any general conclusions deduced will be of importance not only in themselves but also in the further development of the theory and practice of quantitative analysis. From the results for silver chloride discussed above, for example, it appears that the completeness of the precipitation of this salt from aqueous solution is vitally dependent upon the nature and concentration of other chlorides present.

(1907)); experimental analogies place the radical very close to potassium. In preceding solubility comparisons (Kendall and Davidson, *loc. cit.*, p. 989; Kendall and Adler, *loc. cit.*, p. 1480) the ammonium salts have not been included in view of the fact that their melting points are much lower than those of other salts, but here this factor does not come into consideration.

<sup>48</sup> A few isolated and contradictory determinations are given in Seidell, *op. cit.*, p. 609. A single measurement by Forbes indicating that AgCl is only slightly soluble in concentrated ZnCl<sub>2</sub> solutions, which furnishes the sole incongruity in his whole work with the predictions of the present theory, is being further investigated.

Forbes<sup>49</sup> has calculated that the salt is most insoluble in 0.01 *N* chloride solutions; Glowczynski,<sup>50</sup> on the other hand, has found experimentally that the addition of potassium chloride and ammonium chloride in much lower concentrations already involves an appreciable increase above the original solubility value. Evidently the presence of salts of the alkali metals in considerable quantity could easily introduce very significant errors in the analytical procedure at present employed.<sup>51</sup> The magnitude of such errors might, according to the results here obtained, be reduced by the addition of salts of less electropositive metals, but this is a point which requires direct experimental confirmation.<sup>52</sup> Whether the rules outlined in this article could legitimately be expanded to predict the optimum conditions for precipitations in general is a question for future investigation. The available data for other difficultly soluble salts are in few instances sufficiently extensive or reliable to enable us to obtain any such definite indications of the applicability of the generalizations here developed as in the case of silver chloride, but several typical examples are now being more systematically examined, and we hope to report further on this topic shortly.<sup>53</sup>

When the original solute is markedly soluble in water, the effect of the addition of other solutes containing a common ion becomes more complex, and solubility curves with minimum and maximum points may result. Such curves are discussed in the succeeding article, in connection with a study of systems of the type  $HX:HY:H_2O$ . Where the second solute contains no common ion at all (*i. e.*, in systems of the type  $RX:R'Y:H_2O$ ) the equilibria involved naturally present still greater intricacies, as the experience of previous investigators in this portion of the field serves to testify.<sup>54</sup> The satisfactory elucidation of such elaborate systems necessarily awaits the prior formulation of acceptable general rules for systems with a smaller number of variables.

<sup>49</sup> Forbes, *loc. cit.*, p. 1946.

<sup>50</sup> Glowczynski, *ibid.*, p. 172.

<sup>51</sup> Treadwell and Hall, "Analytical Chemistry," 2, 317 (1914).

<sup>52</sup> It is possible that complete precipitation might be ensured only at the expense of introducing other and more significant errors, such as adsorption of added salt by the precipitate.

<sup>53</sup> The particular series under investigation are: (a)  $AgCl$  and  $PbCl_2$  in other chloride solutions, (b) slightly soluble fluorides in  $AgF$  and  $KF$  solutions, (c) the sulfates of the alkaline earth metals in other sulfate solutions, (d) the sulfates and hydroxides of the alkaline earth metals in solutions of more soluble salts of the same metals. These are not mentioned with any intention of reserving the field, but merely to obviate possible duplication of effort.

<sup>54</sup> See the extensive work of Noyes and his collaborators, beginning in *THIS JOURNAL*, 33, 1643 (1911) and continued more recently by Harkins, *ibid.*, 38, 2679 (1916); 41, 1155 (1919).

### General Consideration of Results.

It remains to discuss, somewhat more fully than was done in the introductory section, the validity of the principle adopted as a basis for all of the comparisons here carried out, namely that compound formation between the components is the dominating factor in inducing deviations from ideality in polar solutions. The satisfactory agreement of our predictions with the facts of experiment furnishes in itself, of course, support for this view-point, indicating as it does that the disturbances due to other factors are, in general, subsidiary in their nature. In order to establish this more directly, however, the effect of these factors may here be subjected to brief analysis.

**Internal Pressure.**—Undoubtedly in many of the systems examined in the preceding pages the internal pressures of the components are very unequal. Exact data are not available, but since we know that fused salts, as a class, are far more polar than water and also vary considerably in polar character among themselves, we should expect to find solubilities much below the ideal value in many cases. It has been shown above, however, that the ideal solubility for salts of high melting point in solvents at ordinary temperatures is already practically zero, so that while the internal pressure factor may help to account for abnormally minute solubilities in isolated instances (*e. g.*, silver chloride in water) it can scarcely affect the present argument, which is based upon much larger divergences from the ideal in the opposite direction. True, the possibility exists that the internal pressure effect might increase proportionately with the solubility as compound formation becomes more extensive, but no indications that this is so are found in the present work. It appears, therefore, that under the special conditions here encountered, the internal pressure factor can be neglected.

**Heat of Fusion.**—Owing to the fact that the specific heats of substances in the solid and liquid states are not identical, the factor  $Q$  in Equation I (p. 1485) is not a true constant, even for ideal solutions, but varies with the temperature. The variation thus induced is, however, in general relatively small, and can be omitted without much error. More serious, in non-ideal solutions, is the variation in the differential heat of solution  $Q$  due to interactions between the components on admixture. As is well known, the heat effect of such interactions may be so great in certain aqueous salt solutions as to reverse the sign of  $Q$ , in which case we obtain *decreasing* solubility values with increase of temperature.<sup>55</sup>

This "heat of admixture" factor has been discussed in detail for the case of dilute solutions in an earlier article,<sup>56</sup> to which reference should be

<sup>55</sup> Most calcium salts, for example, exhibit this peculiarity in aqueous solution.

<sup>56</sup> Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2312 (1917).

made. It must be admitted here that the factor is not one which can be definitely correlated with the character of the components, and that consequently the relative positions of the various curves in a series may be very significantly affected, even to the extent of confusing the predicted order of solubilities. This is particularly the case in systems of the type  $RX:H_2O$ , in which heat of admixture variations are very pronounced, and it will undoubtedly be necessary to study the effect of this factor more intensively in the case of such systems before their solubility relationships are satisfactorily established. In systems of simpler types (*e. g.*,  $HX:RX$ ) heats of admixture are in general smaller and more uniform, being positive in sign (the addition compounds formed becoming less stable as the temperature rises) and increasing in magnitude as the extent of compound formation increases. In such series it is unlikely that the relative positions of the curves for different salts with respect to the ideal will be confused by variations in  $Q$ , consequently the comparisons carried out without taking this factor into consideration are still, in most instances, substantially valid.

**Ionization.**—With our views on the ionization of strong electrolytes at present undergoing fundamental modification, it is difficult to treat this factor rigorously. If, on the one hand, we regard the Arrhenius equation  $RX \rightleftharpoons R^+ + X^-$  as valid, and apply to it Nernst's principle of the constancy of the undissociated salt concentration in saturated solutions,<sup>57</sup> then it would follow that the solubility of a salt in an ionizing solvent should exceed the ideal value by an amount immediately calculable from the degree of ionization. For example, in the case of potassium chloride in water (p. 1489), the ideal solubility value 0.00044 at 25° would refer to the undissociated salt only, and correction for ionization<sup>58</sup> would increase it to approximately 0.0025. In other words, the change would not be large and would be in the same direction for all salts. If, on the other hand, we follow Milner and Ghosh in regarding salts as completely ionized both in the solid state and in water solution, no correction of this nature is necessary, although other factors (such as changes in the attractive forces between oppositely charged ions due to changes in the dielectric constant)<sup>59</sup> might enter into consideration.

**Association.**—In the solubility tables shown above,  $\alpha$  (the mol f of solute in the solution) has been calculated from the experiment on the assumption that

molecular types existent in the solution.<sup>60</sup> We do not know the exact association factors for the common solvents, nor the variation in these factors on addition of solute. The necessary correction, nevertheless, will be for any fixed solvent approximately proportional to the concentration of solute unless  $\alpha$  is very large,<sup>61</sup> hence it cannot affect significantly the accuracy of the comparisons here made.

Association of the solute is again a point which it is difficult to discuss at present. If the high association factors quoted for fused salts<sup>62</sup> are accepted, then it is evident that very extensive disassociation must occur as their concentration in a solution diminishes. Changes in the assumed molecular state of the solvent do not, however, change the position of the solubility curve appreciably, as has been shown in a previous article.<sup>63</sup> If, on the other hand, we regard highly polar substances, such as the common inorganic salts, as entirely ionized both in the solid state and in aqueous solution, no need to consider their association ever arises.

**Other Factors.**—The subsidiary effect of other factors (such as atomic volume, valence, etc.,) is being further studied, and will be discussed in a subsequent paper. One point, nevertheless, in connection with valence must be mentioned here. It has been assumed in comparing curves throughout this article,<sup>64</sup> for the sake of simplicity, that the addition compounds formed are of the same monomolecular type AB. Two solutes, however, of different valence character (e. g., a uni-univalent salt  $R'X$  and a uni-divalent salt  $R''X_2$ ) might be expected to give different types of addition compounds with the same solvent B (e. g.,  $R'X, B$  and  $R''X_2, B_2$ ).<sup>65</sup> Since the limiting value which  $X$  approaches at low temperatures for a perfectly stable compound of the type AB is 0.50, while for a compound of the type  $AB_2$  it is 0.33, it is obvious that the relative positions of the solubility curves will not, unless consideration is paid to the variation in type, furnish us with valid information regarding the stability of the compounds.<sup>66</sup> When it is furthermore remembered that in cases where the constituent

<sup>60</sup> For water, for example, at ordinary temperatures, a molecular weight much greater than 18.016 should be employed in accordance with the average molecular type  $(H_2O)_n$ .

<sup>61</sup> At very high concentrations of solute the relative correction necessarily diminishes. Disassociation, furthermore, will be extensive in such solutions.

<sup>62</sup> Kendall and Gross, *THIS JOURNAL*, 43, 1419 (1921).

<sup>63</sup> Booge and Andrews, *ibid.* 30, 2310 (1917). A more detailed treatment

radicals are very diverse in character several different complex addition products between the components may simultaneously be present in a solution,<sup>67</sup> it will not seem remarkable that occasional minor reversals of solubility orders are manifest in the tables presented above. It is a matter for comment, rather, that such divergences from prediction are not more frequent.

**The Electrode Potential Series.**—As a final point, the use of the electrode potential series as the basis for establishing "diversity of radicals" must be justified. Strictly speaking, instead of the experimentally determined electrode-potential values we should employ for each radical what is more fundamental and important, the real "electro-affinity." Until exact free-energy data are more numerous, however, we must be satisfied with the series as it stands, relying on the generally accepted view that it is substantially accurate.<sup>68</sup>

In view of the multiplicity of the disturbing factors discussed above, the question may pertinently be raised (as it was previously against Abegg and Bodländer) whether the generalizations deduced in this work are valid at all. The answer to the question consists in the substantial agreement of the predictions made with the facts of experiment. Criticism can, of course, be readily directed against certain discrepancies, but just as Abegg and Bodländer's general conclusions were not invalidated by the discovery of cases where their predicted solubilities were apparently in error by  $10^6$  or so, in the same way the citation of isolated abnormalities will not suffice to destroy the validity of the arguments here advanced. The justification of the present work lies in the fact that it enables us to obtain a general survey of a very important and intricate subject, with the main features involved duly emphasized. So much having been done, we can now continue more easily with the further development of the topic and with the examination of the remaining factors.

### Summary.

solubility curve

that the predominant disturbing factor is addition compound formation between the components of the solution.

In previous articles it has been established that the extent of such compound formation in any series is dependent upon the diversity in character of the constituent radicals of the components, the basis of diversity being the relative position of the variable radicals in the electrode potential series. Ionization, furthermore, has been found to increase uniformly with compound formation.

These generalizations have here been employed to predict solubility relationships in systems of various types. It has been shown that:

(a) For a fixed solute in a series of different solvents, increasing solubility and increasing compound formation proceed in parallel.

(b) For a series of different solutes of high melting point in a fixed solvent, increasing solubility and increasing compound formation also proceed in parallel at low temperatures.

Illustrations of these rules for non-aqueous and aqueous solutions have been presented which indicate their agreement with the facts of experiment.

A general discussion of solubility relationships in systems of increasingly complex nature (*e. g.*,  $RX:HX$ ,  $RX:H_2O$ ,  $RX:R'X:H_2O$ ) has been made, and the rules deduced for the simpler types of systems have been found to be applicable, to a limited extent, to the more complex types. For example:

(a) Salts of a very weak base exhibit increasing hydrate formation and increasing solubility in water as the acid radical  $X$  diverges from  $OH$ ; salts of a very weak acid show the same behavior as  $R$  diverges from  $H$ .

(b) The increase in the solubility of a difficultly soluble salt in water on addition of a second salt containing a common ion, due to complex salt formation, is dependent upon the diversity of the variable radicals.

The extension of the first of these rules to non-aqueous solutions, and the importance of the second in analytical chemistry, have been noted.

The disturbing effect of other factors upon the ideal solubility curve has been briefly examined, and the possibility of accounting for abnormalities in solubility curves.



[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 367.]

CONDITIONS AFFECTING THE QUANTITATIVE DETERMINATION OF REDUCING SUGARS BY FEHLING SOLUTION.  
ELIMINATION OF CERTAIN ERRORS INVOLVED  
CURRENT IN METHODS.<sup>1</sup>

BY F. A. QUISUMBING AND A. W. THOMAS.

Received March 3, 1921.

The reduction of alkaline cupric solutions by certain sugars has been extensively utilized in qualitative and quantitative analyses of saccharine mixtures since 1841, when Trommer<sup>2</sup> first introduced alkaline copper sulfate as a reagent to distinguish dextrose from sucrose.

Barreswil<sup>3</sup> improved Trommer's reagent by the addition of potassium tartrate which prevented the precipitation of cupric hydroxide, thus increasing the stability of the reagent. Fehling<sup>4</sup> worked out the details of the quantitative method, giving some stoichiometrical equivalents between copper and dextrose. The ratio of 1 molecule of dextrose to 5 of copper was regarded constant by Fehling and was so employed until Soxhlet<sup>5</sup> showed that the ratio was not constant, but varied according to the amount of copper in solution.

The literature relative to modifications of methods of sugar analysis is so voluminous that a detailed discussion cannot be given here. Many of the modifications are described by Browne.<sup>6</sup>

Despite numerous attempts to improve upon the original methods, there is none which will give perfect quantitative results in the analysis of mixtures of common sugars. The errors involved are (1) reducing action of sucrose, (2) "blank" or auto-reduction of Fehling solution, including all modifications of same, and (3) lack of exact control of temperature.

A study of the reducing action of sucrose on Fehling's solution and the effect of the presence of sucrose upon reducing sugars with a view of eliminating the use of empirical formulas and correction tables as a means of correcting for the effect of sucrose is of timely interest.

If the necessity of running "blank" tests to determine the amount of auto-reduction of the Fehling solution (which may be as much as 5 mg.

<sup>1</sup> Part of the thesis submitted by F. A. Quisumbing in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University, 1921.

<sup>2</sup> Trommer, *Ann.*, 39, 360 (1841).

<sup>3</sup> Barreswil, *J. Pharm.*, [3] 6, 301 (1844).

<sup>4</sup> Fehling, *Ann.*, 72, 106 (1849); 106, 75 (1858).

<sup>5</sup> Soxhlet, *J. prakt. Chem.*, [2] 21, 227 (1878).

<sup>6</sup> Browne, "Handbook of Sugar Analysis," John Wiley & Sons, 1912.

of cuprous oxide and is not constant) could be dispensed with, it is admitted that greater accuracy and speed would be realized.

In all methods the reaction between reducing sugars and the complex cupric compound is carried out at the indefinite temperature obtained by heating in a bath of boiling water, or boiling the mixture directly over a flame. It is evident that since the amount of reduction varies with the temperature and time of digestion, errors are unavoidable due to changes in barometric pressure. Further, the methods involving direct boiling of the mixture are subject to an additional lack of accuracy due to the difficulty in determining exactly when the solution begins to boil. Apart from the inaccuracy of this sort of procedure, the manipulator is obliged to give his constant attention during the boiling.

The purpose of this investigation is to establish conditions for the use of a Fehling solution in the quantitative analysis of common sugars such that the errors due to atmospheric pressure fluctuations and temperature of digestion, difficulty in observation of exact time of boiling, surface oxidation, auto-reduction of Fehling solution, and reducing action of sucrose might be eliminated or reduced to a minimum.

### Sugars Used.

Solutions for measurement of optical rotation were made in all cases by dissolving 5 g. of the sugar in distilled water and adjusting to 100 cc. at 25°. The solutions were allowed to stand until optical equilibrium had been attained before polarization.

A Schmidt and Haensch polarimeter, sensitive to 0.01° angular scale was employed, the solutions in 2 dm. tubes being maintained at 25°  $\pm$  0.01°, by use of the thermostat described by Nelson and Beegle.<sup>7</sup>

Unpurified sodium flame, and the light of a mercury vapor lamp passed through Wratten No. 74 filter, giving a wave length,  $\lambda = 546\mu\mu$ ,<sup>8</sup> were used as sources of light.

**Sucrose.**—Bureau of Standards, Sample No. 17. Analysis showed: moisture 0.003%; ash, 0.003%. No reducing action was shown by 400 mg. of this sugar on Fehling solution at 80° during 30 minutes. Specific rotatory power,  $[\alpha]_{\lambda=546}^{25} = 78.200^\circ$ ;  $[\alpha]_D^{25} = 66.405^\circ$ .

**Dextrose.**—A specimen of the Corn Products Refining Company's c. p. Dextrose, was purified according to the Bureau of Standards method.<sup>9</sup> Analysis of this pure sample showed: moisture, 0.150%; ash, 0.003%. Specific rotatory power,  $[\alpha]_{\lambda=546}^{25} = 62.021^\circ$ ;  $[\alpha]_D^{25} = 52.480^\circ$ .

**Levulose.**—A white crystalline specimen kindly furnished by Prof. J. M. Nelson was recrystallized from conc. acetic acid solution as recommended by Hudson and Dale<sup>10</sup> for dextrose. The sample after drying *in vacuo* over saturated sodium hydroxide solution showed: moisture, 0.002%; ash, 0.060%. Specific rotatory power,  $[\alpha]_{\lambda=546}^{25} = -105.30^\circ$ ;  $[\alpha]_D^{25} = -89.40^\circ$ .

<sup>7</sup> Nelson and Beegle, *THIS JOURNAL*, 41, 559 (1919).

<sup>8</sup> W. C. Vosburgh, *ibid.*, 42, 1698 (1920).

<sup>9</sup> Bur. Standards, *Circ.*, 44, 92 (1919).

<sup>10</sup> Hudson and Dale, *THIS JOURNAL*, 39, 320 (1917).

**Invert Sugar.**—The invertase method of preparation was tried and found unsatisfactory for our purpose because of the formation of an insoluble copper compound when the residual invertase was heated with Fehling solution. This is the so-called "copper yeast gum" (Salkowski<sup>11</sup>), also mentioned by Nelson and Born.<sup>12</sup> For these reasons the invert sugar solution was prepared by mixing equal numbers of molecules of dextrose and levulose. Specific rotatory power,  $[\alpha]_{\lambda=546}^{25} = -21.50^\circ$ ;  $[\alpha]_D^{25} = -18.39^\circ$ .

**Lactose.**—Squibb's pure lactose was dissolved in boiling distilled water and when cold, a mixture of equal volumes of ether and alcohol was added. The lactose crystallized from this solution, washed with alcohol and ether, was dried *in vacuo* at  $70^\circ$ . This dried material was ground and dried further at  $100^\circ$  for 4 to 5 hours. Analysis showed it to contain: moisture (loss at  $125^\circ$  to  $130^\circ$ ), 5.22%; ash, 0.03%. Specific rotatory power,  $[\alpha]_{\lambda=546}^{25} = 61.36^\circ$ ;  $[\alpha]_D^{25} = 52.90^\circ$ .

**Maltose.**—This sugar was prepared from Lintner<sup>13</sup> soluble starch by saccharification of the starch with highly purified malt amylase kindly furnished by Professor H. C. Sherman. The product of the saccharification was fermented by a pure culture of *Saccharomyces Ludwigii* to remove fermentable sugars other than maltose. Upon completion of fermentation, the solution was heated in an autoclave, cooled and the dextrins precipitated by alcohol. The filtrate was evaporated *in vacuo* to a thin syrup, which upon inoculation with a few maltose crystals yielded a crop of crystals which were recrystallized from hot 95% alcohol, using acid-purified cocoanut charcoal as decolorizing agent. This maltose was dried *in vacuo* at  $60^\circ$  for 4 hours, ground to powder and further dried at  $90^\circ$  for 10 hours. The final product contained: moisture, 5.05%; ash, 0.02%. Specific rotatory power,  $[\alpha]_{\lambda=546}^{25} = 153.75^\circ$ ;  $[\alpha]_D^{25} = 131.25^\circ$ .

### Atmospheric Pressure and Temperature of Boiling.

Irregularity of results due to the effect of fluctuations of atmospheric pressure on temperature of boiling has been reported by several investigators.<sup>14</sup> A series of experiments conducted in this laboratory at different times of the year under barometric pressures varying from 753 mm. to 760 mm. lend support to the above findings. The reducing power of 100 and of 150 mg. of dextrose determined by the 2-minute boiling over a flame and the 12-minute digestion in boiling water varied 2% between the atmospheric pressures mentioned.

It is apparent that variation in boiling point due to ordinary changes in atmospheric pressure and also due to location of laboratories at different altitudes may seriously affect the accuracy of results obtained by the reduction methods in common use.

To overcome the uncertainties of temperature in all experiments cited herein, a thermostat was used in which water served as the liquid medium for temperatures below  $90^\circ$ , and rapeseed oil for higher temperatures.

<sup>11</sup> Salkowski, *Z. physiol. Chem.*, 31, 305 (1900).

<sup>12</sup> Nelson and Born, *THIS JOURNAL*, 36, 393 (1914).

<sup>13</sup> Lintner, *J. prakt. Chem.*, [2] 34, 378 (1886).

<sup>14</sup> Traubagen and Cobleigh, *THIS JOURNAL*, 21, 369 (1899). Rosenkranz, *Z. ver. Deut. Zuckerind.*, 61, 426 (1911). Maquenne, *Compt. rend.*, 161, 617 (1915); 162, 145 (1916).

### Influence of Temperature and Time of Heating.

The results of a series of experiments to determine the most suitable temperature and length of time of heating for the oxidation of the sugars by a Soxhlet-Fehling solution are plotted in Figs. 1 and 2. The solution consisted of 50 cc. of mixed Soxhlet-Fehling<sup>15</sup> solution and 50 mg. of glucose, the volume being adjusted to 100 cc. with distilled water.

Upon critical examination of the curves in Figs. 1 and 2, it is seen that temperature and time of heating exert a great influence on the oxidation of dextrose. Reduction increases with rise of

REDUCTION BY GLUCOSE AT DIFFERENT TEMPERATURES

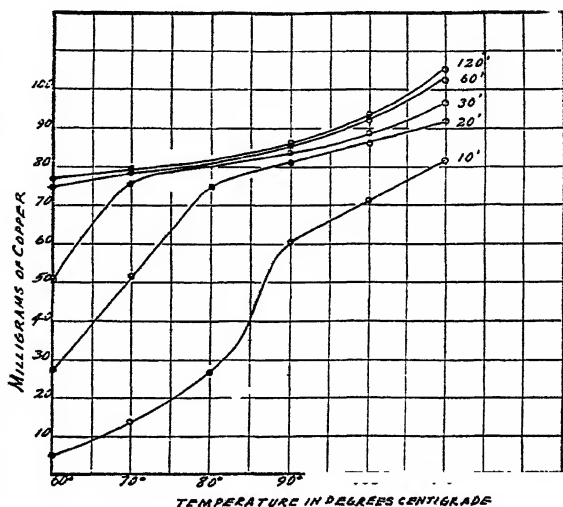


Fig. 1.

CURVES SHOWING THE INFLUENCE OF TIME ON REDUCTION BY GLUCOSE

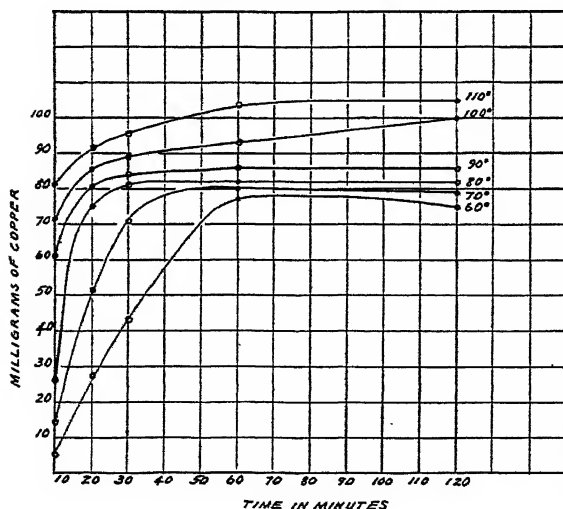


Fig. 2.

temperature and it appears complete at temperatures below 90° after an hour's heating. At temperatures above 100° there is an appreciable increase in reduction which may be due to auto-reduction of Fehling solution.

The curves in Fig. 3 show that Soxhlet-Fehling solution is reduced at high temperatures when no sugar is present. The detection of cuprous oxide in so-called traces in the "blanks" by

<sup>15</sup> Soxhlet's formula: (A) 34.639 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 500 cc. of solution; (B) 173 g. of Rochelle salt, and 51.6 g. of NaOH in 500 cc. of solution.

methods of 2 minutes boiling over a flame or heating in boiling water is due to this auto-reduction of Fehling solution. Attention is called to the absence of such auto-reduction at 80° for periods of heating up to 30 minutes, and furthermore that at this temperature there is but slight formation of cuprous oxide even after heating for 1 hour.

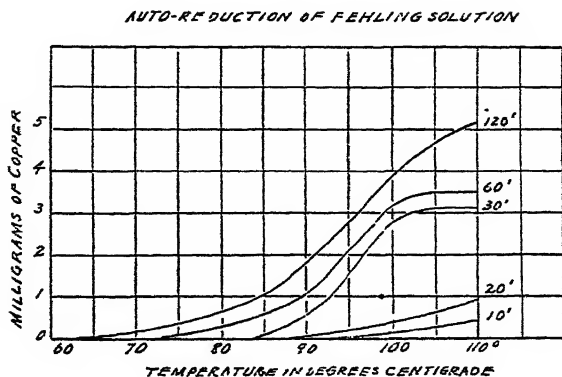


Fig. 3.

is but slight formation of cuprous oxide even after heating for 1 hour.

### Reducing Action of Sucrose on Fehling Solution.

A study of the effect of sucrose in the presence of reducing sugars has been made by Maquenne,<sup>16</sup> Pellet,<sup>17</sup> Saillard,<sup>18</sup> Browne<sup>19</sup> and others, but no definite efforts have been made to eliminate its reducing action on Fehling solution.

Experiments show that when the current methods of heating are used, the error in the glucose and invert sugar determinations, when sucrose is present is considerable. Browne<sup>20</sup> gives an empirical formula for the correction of errors due to reducing action of sucrose on glucose. Meissl and Hiller<sup>21</sup> give tables of factors for calculating copper to invert sugar for different ratios of sucrose to invert sugar. Munson and Walker<sup>22</sup> give tables for the determination of invert sugar and lactose in the presence of sucrose.

The inadequacy of the use of these tables, factors for correction, empirical formulas and other unnecessary calculations involved, led to the following study of the comparative action of sucrose on Fehling solution with the view of establishing the best conditions by which the reducing action of sucrose could be entirely eliminated or reduced to a minimum.

<sup>16</sup> Maquenne, *Compt. rend.*, 162, 207, 145 (1916); 161, 617 (1915).

<sup>17</sup> Pellet, *Ann. Chem. Anal.*, 20, 169 (1915); *Bull. Assoc. Chem. suc. dist.*, 31, 183 (1913-14).

<sup>18</sup> Saillard, *Compt. rend.*, 161, 591 (1915); *J. Fabr. suc.*, 56, 1 (1915).

<sup>19</sup> Browne, *THIS JOURNAL*, 28, 439 (1906).

<sup>20</sup> Browne, "Handbook of Sugar Analysis," 1912, p. 428.

<sup>21</sup> Meissl and Hiller, *Z. Ver. Deut. Zuckerind.*, 39, 735 (1889).

<sup>22</sup> Munson and Walker, *THIS JOURNAL*, 28, 663 (1906).

From the curves in Fig. 4 it is apparent that the reducing action of sucrose is considerable when current methods are used. The amount of copper reduced mounts rapidly with increase in concentration of sucrose.

The reducing values plotted in the above figure were all corrected for "blank" reductions.

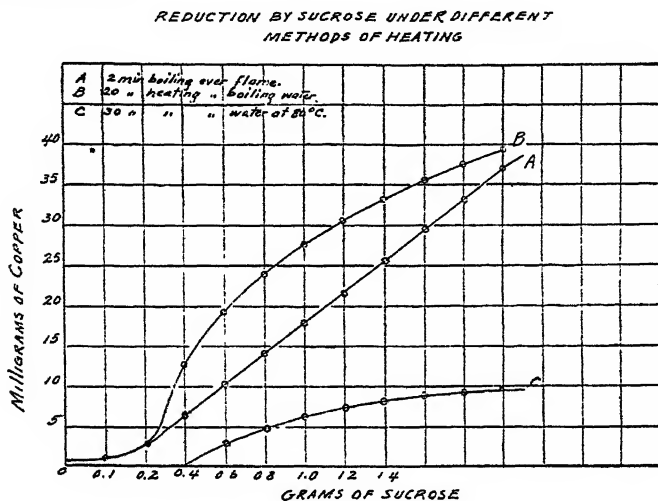


Fig. 4.

### Selection of Conditions for Reduction.

If it were feasible to determine when the process of reduction is complete, that point would be the most appropriate one at which to terminate the treatment, but when the time element is considered, it does not matter whether the terminal point is reached for the purpose of testing an analytical method. By selecting a set of standardized conditions such that the amount of reduction obtained is sharply defined at a selected point, that point may successfully be used as a terminal point. Upon critical study of the curves in Figs. 2 and 3, the conditions of 80° and 30 minutes appear to be most ideal, because (1) Fehling solution at this temperature and time of heating does not give a "blank" reduction; and (2) beyond 30 minutes heating at 80° the curve rises very slightly. This point can therefore be safely called the "terminal point." Temperatures other than 80° might have been selected, but a lower temperature would require a longer time of heating to give a reasonable amount of copper for quantitative determination, and at higher temperatures the difficulty of accurately maintaining the temperature of the bath interferes with the accuracy of short-time digestions.

Objection may be raised that 30 minutes' reduction involves too much time for the analysis, but experience has proved that when sets of 7 samples

are run under these conditions, the reducing power of a sample can be determined within 8 to 10 minutes from the time the sample is placed in the bath to the completed washing of the precipitated cuprous oxide.

A great advantage claimed for this method over the procedure of boiling over a flame is that continuous observation to determine the time boiling is not required. Furthermore, this method offers an important improvement over the current methods in the complete elimination of auto-reduction of Fehling solution; and as shown in Fig. 4, the presence of as much as 425 mg. of sucrose has no effect on the accuracy of the process. We find also that a long time of heating produces a coarse granular cuprous oxide which is easily washed and removed from the beaker without the aid of a rubber "policeman."

### Apparatus and Procedure.

**Thermostat.**—A 50-liter constant-temperature bath, similar to the one described by H. C. Sherman and A. W. Thomas,<sup>23</sup> and J. M. Nelson and F. M. Beegle<sup>7</sup> was constructed. The temperature was maintained at  $80^{\circ} \pm 0.1^{\circ}$ . Excessive evaporation of the water was prevented by the addition of 2 or 3 drops of colorless paraffin oil.

**Procedure.**—When the bath had attained proper temperature, a 350-cc. beaker containing the solution to be tested was placed in it, supported on an iron ring, so that the levels of the liquid in the container and the water in the bath were practically identical. Occasionally the beaker was shaken and the solution rotated to ensure thorough mixing. At the end of the desired time of heating, the beaker was removed, and the solution containing the precipitated cuprous oxide filtered through a mat of asbestos in a Gooch crucible. The precipitate was washed with warm water, then dissolved with 10 to 20 cc. of 16 *N* nitric acid, and copper determined either by Beans and Stillman's<sup>24</sup> electrolytic method or E. C. Kendall's<sup>25</sup> modified iodide method.

### Fehling Reagent.

As a result of Nef's<sup>26</sup> work we know that the sugar molecule in the presence of Fehling solution undergoes oxidation, reduction, condensation or further decomposition giving rise to a great multiplicity of aldehydes and acids as end products, the kinds, as well as amounts of which, vary with concentration of sugar and of alkali used.

<sup>23</sup> Sherman and Thomas, *THIS JOURNAL*, 37, 623 (1915).

<sup>24</sup> J. W. Stillman, "New Direct Method for the Electrolytic Determination of Copper," *Dissertation*, Columbia Univ., 1920.

<sup>25</sup> Kendall, *THIS JOURNAL*, 33, 1947 (1911).

<sup>26</sup> Nef, *Ann.*, 357, 214 (1907); 376, 1 (1910); 403, 204 (1914).

**Influence of the Nature of the Alkali.**—The nature and amount of alkali in Fehling solution influence both reduction and the physical character of the copper oxide formed. Sodium hydroxide and potassium hydroxide solutions of equivalent concentrations give practically the same reduction with dextrose and invert sugar. Glendinning<sup>27</sup> finds that maltose shows a higher reducing power when potassium hydroxide is substituted for sodium hydroxide in Fehling solution. Kjeldahl<sup>28</sup> studying the effect of different strengths of sodium hydroxide solution upon reduction, found that between limits of 0.5 to 2 *N* sodium hydroxide solution, the variation was not more than 1% with glucose, while with maltose and lactose there was a wide variation.

It is our experience that Fehling solution containing sodium hydroxide gives a more satisfactory precipitation than when potassium hydroxide or the carbonates are used. The curves in Fig. 5 illustrate the influence

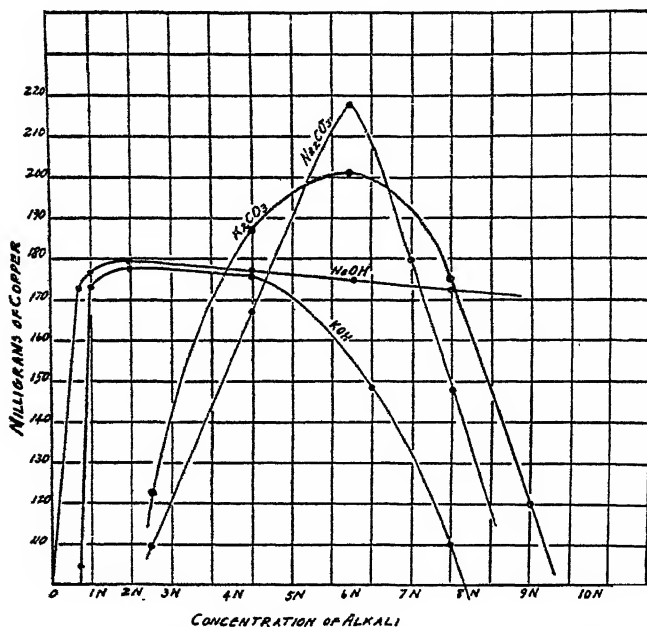


Fig. 5.—The influence of different alkalis in Fehling solution on the oxidation of glucose.

of kind and concentration of alkali upon the oxidation of glucose by Fehling solution.

**Influence of Concentration of Alkali.**—According to Fig. 6 the most effective alkalinity of Fehling solution is 1.6 *N* in terms of sodium hy-

<sup>27</sup> Glendinning, *J. Chem. Soc.*, 67, 999 (1895).

<sup>28</sup> Kjeldahl, *Compt. rend. trav. Laboratoire Carlsberg*, [1] 4, (1895).



dioxide. This alkalinity has also been found best by Kjeldahl<sup>28</sup> and Brown, Morris and Millar,<sup>29</sup> when reduction was carried on in a boiling-water-bath. Fehling solution, of this alkalinity corresponds to 65 g. of sodium hydroxide in 500 cc. of the alkaline tartrate solution.

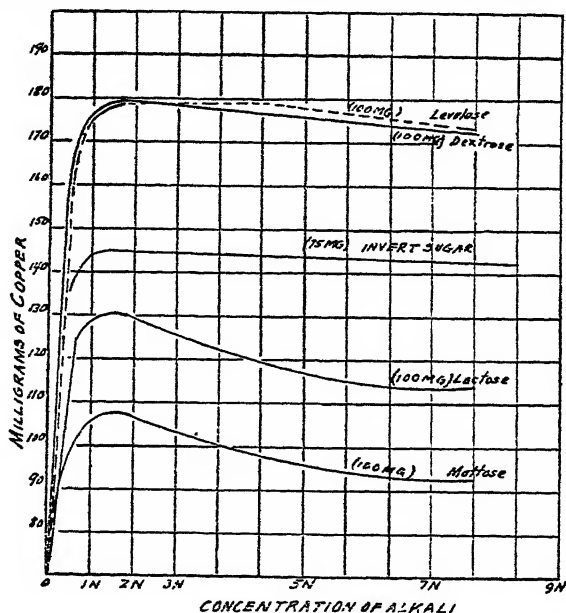


Fig. 6.—The influence of different concentrations of alkali in Fehling solution on the oxidation of sugars.

The curves show that the concentration of hydroxyl ions influences the rate and amount of oxidation of the sugars. The amount of copper reduced increases with increasing concentration of hydroxyl ions up to a certain point, where oxidation appears to be at its maximum, and from that point further increase in hydroxyl ions tends to decrease reduction. The most plausible explanation for this is that the decrease in reduction is due to the formation in large quantities of compounds of lower reducing power. The same phenomenon is exhibited regardless of the nature of alkali. Greater decomposition of the sugar is more apparent with lactose and maltose.

**The Effect of Varying the Amount of Copper Sulfate in Fehling Solution.**—To determine this effect a test solution consisting of 50 cc. of Fehling solution containing various amounts of copper sulfate, 3.2 g. of sodium hydroxide, 8.65 g. of the sodium potassium tartrate and 100 or 200 mg. of the sugar was used. The total volume of the solution was adjusted to 100 cc. with distilled water in each case.

<sup>29</sup> Brown, Morris and Millar, *J. Chem. Soc.*, 71, 96 (1897).

TABLE I.

OXIDATION OF REDUCING SUGARS BY FEHLING SOLUTION CONTAINING VARIOUS AMOUNTS OF COPPER SULFATE, AT 80° FOR 30 MINUTES.

Wt. of Cu in 50 cc. Mg.	Ratio of NaOH to Cu by weight.	Reduction in terms of mg. of Cu.						Blank.
		Dextrose.		Levulose.		Lactose.		
		100 mg.	200 mg.	100 mg.	200 mg.	100 mg.	200 mg.	
210	15.2:1	142.6	...	...	...	108.7	...	0
315	10.0:1	148.3	...	152.6	...	114.4	...	0
420	7.6:1	152.9	225.9	154.5	304.6	118.0	224.7	0
525	6.2:1	156.1	303.4	157.0	308.8	119.6	227.9	0
630	5.0:1	158.8	307.9	158.9	312.3	120.5	232.6	0.3
840	4.0:1	157.6	311.8	158.6	314.3	121.7	233.4	0.9
1050	3.0:1	155.8	311.1	157.7	311.4	120.7	232.1	3.0
1260	2.4:1	150.2	307.0	154.6	309.6	97.7	226.1	3.9

TABLE II.

OXIDATION OF DEXTROSE IN THE PRESENCE OF SUCROSE BY FEHLING SOLUTION CONTAINING VARIOUS AMOUNTS OF COPPER SULFATE.

Reduction By Dextrose Alone.

Wt. of Cu in Fehling sol. Mg.	Reduction in terms of mg. of Cu.			
	Mg. of dextrose in 10 cc. of solution.			Blank.
	5 mg.	50 mg.	95 mg.	
525	17.8	161.0	297.8	0
630	17.6	160.8	299.2	0.3
840	19.2	157.2	297.2	0.9
1050	18.5	155.8	291.3	3.0
1260	17.5	151.8	287.4	3.5

REDUCTION OF DEXTROSE IN THE PRESENCE OF SUCROSE.

Reduction in terms mg. of Cu.

	5 mg. Dextrose. 50 mg. Dextrose. 95 mg. Dextrose.		
	95 " Sucrose. 50 " Sucrose. 5 " Sucrose.		
	5 mg. Dextrose. 95 " Sucrose.	50 mg. Dextrose. 50 " Sucrose.	95 mg. Dextrose. 5 " Sucrose.
525	17.8	161.0	297.6
630	20.2	161.0	299.4
840	21.1	159.0	296.8

Upon examination of Tables I and II, the most suitable ratio is seen to be from 5 to 6 of sodium hydroxide to 1 of copper by weight. In other words, with the alkalinity of 1.6 *N* (3.2 g. of sodium hydroxide per 50 cc. of mixed reagent), 0.525 to 0.630 g. of copper gives the most satisfactory reduction. It is also interesting to note that with increasing concentration of copper sulfate, total reduction is decreased, while auto-reduction of the solution is increased. Furthermore, Table II shows that in the presence of sucrose, increasing the concentration of copper sulfate tends to increase reduction. It seems therefore that concentration of copper has a direct bearing on the decomposition of sucrose. If enough reducing sugar is present to precipitate nearly all of the copper in Fehling solution, the presence of sucrose plays no part in the reduction.

**The Effect of Varying the Amount of Sodium Potassium Tartrate in the Presence of Constant Amounts of Alkali and Copper Sulfate.**—The test solution consisted of 25 cc. of copper sulfate solution containing 525 mg. of copper (as cupric sulfate), 3.2 g. of sodium hydroxide, 100 mg. of the sugar and various amounts of tartrate. The volume of each solution was made up to 100 cc. with distilled water.

A saturated solution of sodium potassium tartrate was prepared from a commercial Rochelle salt (Highest Purity), and filtered. To the clear solution, 95% alcohol was added with constant stirring, and the salt was allowed to crystallize. The crystals were washed with alcohol, and dried in an oven at 50° for 15 hours, and then at 60° to 65° for 10 hours. The salt as analyzed contained 4 molecules of water of crystallization.

TABLE III.  
INFLUENCE OF CONCENTRATION OF ROCHELLE SALT.

Weight of Rochelle salt.	Mg. of copper reduced.			
	Dextrose.	Levulose.	Lactose.	Maltose.
G.				
7.96	159.0	155.4	112.3	90.3
8.65	159.5	154.2	112.9	92.5
11.38	158.8	155.3	113.1	93.0
15.84	157.7	154.0	112.5	92.6
17.30	155.3	155.0	112.6	92.8

Table III shows that there is no material effect of increasing the concentration of the tartrate beyond that called for by the Soxhlet-Fehling formula. The formation of the complex cupric tartrate ion is assured by the presence of 8.65 g. of Rochelle salt in 50 cc. of the mixed Fehling solution. Less than this amount appears to give less reduction for lactose and maltose. The reduction by dextrose decreases with increasing concentration of the tartrate while with levulose there is no appreciable effect of increasing amounts of tartrate upon the reduction.

**Photosensitiveness and Keeping Quality.**—The photosensitiveness of Fehling solution as evidenced by the precipitation of cuprous oxide upon exposure of the solution to light was noticed by Fehling<sup>4</sup> and numerous other investigators<sup>30</sup> have confirmed this.

Our experiments show that 50 cc. of mixed Fehling solution exposed to direct sunlight will give traces of cuprous oxide precipitate within 10 to 20 hours, while if kept in the dark, or in opaque bottles, or in ray-filter solutions such as potassium dichromate, or acidified quinine sulfate, decomposition does not take place until after a month or longer. 50 cc. of mixed Fehling solution exposed to direct sunlight will be completely

<sup>30</sup> Eder, *Sitzungsber. Akad. Wiss., Wien*, 92, 344 (1885); through *J. Phys. Chem.*, 17, 204 (1913); Byk, *Z. physik. Chem.*, 49, 659, 679 (1904); Leighton, *J. Phys. Chem.*, 17, 204 (1913).

decolorized after 2 months, showing then only a slight amount of copper present.

Fehling solution as ordinarily prepared shows a slight tendency to auto-reduction.

Munson and Walker<sup>31</sup> contended that unless the spontaneous reducing power of the alkaline tartrate solution is determined and allowed for, the results obtained will be considerably too high. In their original article<sup>22</sup> Munson and Walker gave a series of figures showing the reducing power of their alkaline tartrate solution from day to day during the course of their investigation. The results varied from  $-0.8$  to  $+1.6$  mg. of cuprous oxide.

Our experiments with Fehling solutions of varying copper, tartrate and alkali content show conclusively that the reducing power of the solutions is not entirely due to impurities of the alkaline tartrate solution as generally claimed, but to a great extent to the method of heating. Samples of Fehling solution prepared according to the formula given in page 1520, showed no reducing power when heated at  $80^{\circ}$  for 30 minutes, *i. e.*, no "blank," after they had been kept in the dark for 5 months; but, if reduction was carried out according to Munson and Walker's method, the solutions gave a considerable precipitate, which varied from 1.5 to 4.0 mg. of copper.

### Colloidal Cuprous Oxide.

When a reducing sugar is treated with an alkali, a series of degradation products is formed, and these are responsible for the reduction of the cupric salt. The cuprous oxide precipitate that comes down first in the hydrate form has different degrees of dispersion. The different colors of the same chemical compound,  $\text{Cu}_2\text{O}$ , when in the colloidal state, are claimed by Svedberg<sup>32</sup> and Wo. Ostwald<sup>33</sup> to be nothing more than the color changes coincident with the gradual increase of the size of the particles, the red being the largest.

Experiments performed in this laboratory show that the concentration of the reducing substance, nature of the alkali, and the degree of alkalinity of the latter, temperature and time of heating influence the production and physical character of cuprous oxide. The "colloidal" particles are produced even at 6 *N* alkalinity with the carbonates, while with the alkali hydroxides, the same dispersions are noticeable only at concentrations below 0.5 *N*. Reduction at high temperatures augments the production of the "colloidal" copper oxide. Low temperature and a fairly high con-

<sup>31</sup> Munson and Walker, *THIS JOURNAL*, 29, 541 (1907).

<sup>32</sup> Svedberg, "Herstellung Kolloider Lösungen," Steinkopff, 1920.

<sup>33</sup> Wo. Ostwald, *Kolloidchem. Beihefte*, 2, 409 (1911).

centration of alkali in Fehling solution increase the size characteristic of the red cuprous oxide.

### Surface Oxidation.

The size and shape of receptacles in which the mixture of Fehling solution and sugars are heated have an effect on the amount of copper reduced. Also the nature of the material of which the receptacle is made has an influence upon the velocity of deposition of cuprous oxide.<sup>28,34,35</sup>

While an appreciable loss of cuprous oxide is known to result from surface oxidation, no attempt has been made to correlate surface area of the reagent exposed to the walls of the glass container and reduction. To get definite figures for such relationship, the following experiments were made. They were performed in beakers where the surface of the reagent was exposed to direct action of the air. The solution consisted of 200 mg. of the sugar and 50 cc. of Fehling solution, made up to 100 cc. with distilled water.

Table IV shows that reduction is directly proportional to lateral area of liquid exposed to the glass and inversely proportional to surface area of liquid exposed to the air. That is, the more surface area of the liquid exposed to the air, the less the amount of copper reduced. Boiling for 2 minutes over a flame gives reduction which varies to the extent of 5.8 mg. of copper with beakers in which the surface area of the liquid exposed to the air ranged from 43.7 to 85.6 sq. cm. Heating for 20 minutes in boiling water gives a difference of 3.2 mg. and for 30 minutes in water at 80°, 2.9 mg. It should be observed that in all these three methods of heating 350 and 550 cc. beakers gave practically the same reduction, although the surface areas of the liquid exposed to the air differed by 13.3 sq. cm. This is due to the fact that their *total surface areas* ( $2\pi rh + \pi r^2$ ) are equal.

A second series of experiments was planned in order to study this relationship further. The solutions consisted of 100 mg. of dextrose and 50 cc. of Fehling solution, made up to 100 cc. with distilled water. In (1) the liquid was covered with a layer of toluene, (2) the beakers were covered with watch glass, and in (3) the liquid was left exposed to the air. Copper was determined electrolytically.

Table V shows that when the action of air is excluded, reduction is proportional not to *total* but to *lateral* area of liquid exposed to the glass; that is, the higher the column of liquid exposed to the glass surface, the more cuprous oxide is precipitated. It appears that the most plausible explanation for this phenomenon is that reduction is accelerated more along the sides than at the bottom of the container because as the precipitate

<sup>34</sup> Urecht, *Bér.*, 15, 2687 (1882).

<sup>35</sup> Kendall, *THIS JOURNAL*, 34, 317 (1912).

drops down from the sides to the bottom, the layer of cuprous oxide thus formed tends to cut down the accelerating effect of the glass surface at the bottom, and leaves a free surface along the sides for catalytic action. The table also shows that the amount of cuprous oxide lost due to surface oxidation is proportional to the area of liquid exposed to the air.

TABLE IV.

EFFECT OF SURFACE AREA OF LIQUID EXPOSED TO THE AIR AND LATERAL AREA OF LIQUID EXPOSED TO THE GLASS ON THE AMOUNT OF COPPER REDUCED.

(200 Mg. of Dextrose Used in Each Case.)

Receptacle.	Cc.	Diameter. Cm.	Height of column of liquid. Cm.	Lateral area liquid exposed to glass. Sq. Cm.	Surface area of liquid exposed to air. Sq. Cm.	Methods of heating.		
						2 min. boiling over a flame.	20 min. heating in boiling water.	30 min. heating in water in 80°.
Beaker	750	10.0	2.0	65.2	85.6	305.0	304.7	302.9
"	550	9.5	2.7	79.5	70.1	305.8	306.4	304.6
"	350	8.5	3.5	92.2	56.8	305.7	306.7	304.7
"	250	7.5	4.0	93.0	43.7	310.8	307.0	305.8
Flask	250	9.8	3.0	89.4	70.4	306.7	310.2	304.5
Erlenmeyer								

The figures represent averages of duplicate determinations which varied not more than 0.7 mg. of Cu.

TABLE V.

(100 Mg. of Dextrose Used in Each Case.)

Beaker.	Diameter.		Height of column of liquid.	Lateral area of liquid exposed to glass.	Surface area of liquid exposed to air.	(1) Covered with toluene.	(2) Covered with watch glass.	(3) Uncovered.	Loss. (1) — (3).
Cc.	Cm.	Cm.	Sq. Cm.	Sq. Cm.					
1000	12.0	1.7	63.2	111.6	196.7	196.3	191.6	5.1	
350	8.5	3.5	92.2	56.8	198.7	198.2	196.2	2.5	
140	6.25	5.5	110.8	36.0	199.4	200.9	198.8	0.6	

The figures represent averages of duplicate determinations which varied not more than 0.4 mg. of Cu.

The effect of surface oxidation was further investigated by adding to definite weights of chemically pure cuprous oxide, 50 cc. of Fehling solution and making the total volume of the solution up to 100 cc. with distilled water, and transferring to 350 cc. beakers of same diameters. One cc. of toluene was added to each. After the mixtures had been heated for 30 minutes in water at 80°, the cuprous oxide was filtered off, washed and copper determined electrolytically.

	Covered with toluene. Mg.	Covered with watch glass. Mg.	Uncovered. Mg.	
Weight of $\text{Cu}_2\text{O}$ used.....	147.9	234.2	230.6	239.6
" " " recovered.....	147.8	234.0	227.2	237.0

Cuprous oxide used and recovered was calculated from the weight of copper determined electrolytically.

These experiments show that the loss of cuprous oxide due to surface oxidation can be obviated by either covering the liquid with some inert liquid such as toluene, or by covering the beaker with a watch glass. The latter serves to prevent evaporation of the liquid as well as surface oxidation. Kjeldahl<sup>28</sup> eliminated this error by use of an atmosphere of hydrogen or of oxygen-free illuminating gas. Although Kjeldahl's method undoubtedly gives more nearly the true reduction, the inconveniences attending such manipulation would preclude its general use. Covering the beaker with a watch glass approximates quite as well the true reduction as the other expedients suggested, and, of course, is preferable because of its simplicity.

### Mutual Effect of Sucrose and Reducing Sugars.

Earlier in this discussion it was noted that under the newly proposed conditions the presence of as much as 425 mg. of sucrose had no reducing action on the modified Fehling solution.

The reducing action of sucrose was further investigated by running reductions with different mixtures of sucrose and reducing sugars. The effects are shown in the tables following. In these tables the amounts of reducing sugar are to be found in the first column and the weights of sucrose mixed with the different amounts of reducing sugar are given in the top horizontal line. The figures given in the second column are the amounts of cuprous oxide precipitated by the respective amounts of reducing sugar, expressed in terms of milligrams of copper, while in the remaining columns is given excess reduction caused by the presence of the sucrose.

TABLE VI.  
REDUCTION BY MIXTURES OF SUCROSE AND DEXTROSE.

Dextrose Mg.	Sucrose in Mg.						
	0.	400.	600.	800.	1000.	1500.	2000.
0	0	0	3.0	3.4	6.2	8.7	9.3 mg. Cu
20	42.2	0	3.3	3.6	5.9	11.0	14.1
50	102.3	0	3.7	5.0	5.1	10.8	12.0
100	201.2	0	3.7	4.2	5.3	10.5	11.0
150	295.2	0	3.3	4.4	4.3	9.2	11.1
200	385.1	0	3.1	4.5	3.9	8.4	10.6
250	472.7	0	3.0	3.7	3.6	4.3	10.2

TABLE VII.  
REDUCTION BY MIXTURES OF SUCROSE AND LEVULOSE.

Levulose. Mg.	Sucrose in Mg.						
	0.	200.	300.	400.	500.	1000.	2000.
0	0	0	0	0	2.1	6.2	9.3 mg. Cu
10	19.0	0	1.2	2.3	3.3	9.3	13.8
40	75.5	0	2.6	3.7	4.6	9.5	12.5

TABLE VII.—(Continued).

Levulose Mg.	0.	200.	300.	400.	500.	1000.	2000.
80	150.5	0	1.2	2.5	4.2	6.6	11.2
120	220.2	0	1.6	3.3	5.1	7.9	12.3
160	291.8	0	0.2	1.5	3.8	6.8	11.5
200	360.6	0	0.2	0.5	2.8	4.9	10.9
240	428.1	0	0.1	0.8	2.0	4.3	11.0

TABLE VIII.

## REDUCTION BY MIXTURES OF SUCROSE AND INVERT SUGAR.

Invert Sugar. Mg.	Sucrose in mg.						
	0.	200.	300.	400.	500.	1000.	2000.
0	0	0	0	0	2.1	6.2	9.3 mg. Cu
10	20.0	0	1.7	2.5	3.1	11.4	19.2
20	39.1	0	1.9	2.3	3.2	11.1	19.1
40	79.5	0	1.0	0.4	2.4	8.3	16.4
80	154.6	0	0.5	0.6	2.0	7.5	16.3
120	229.3	0	1.1	0.5	1.7	6.6	16.1
160	301.5	0	0.4	1.1	2.1	5.6	16.6
200	373.0	0	0.0	0.0	0.1	3.9	13.0
240	441.5	0	0.2	0.0	0.0	4.0	11.2

TABLE IX.

## REDUCTION BY MIXTURES OF SUCROSE AND LACTOSE.

Lactose. Mg.	Sucrose in Mg.				
	0.	200.	500.	1000.	2000.
0	0	0	2.1	6.2	9.3 mg. Cu
10	12.2	0.8	1.5	7.2	16.3
50	61.5	1.4	3.4	9.0	18.6
100	123.0	1.5	3.4	9.3	18.6
150	184.5	1.5	3.5	9.7	18.9
200	246.0	1.6	3.2	9.9	18.4
250	307.1	0.6	3.4	8.3	17.7
300	368.0	0.3	3.2	8.3	16.5
350	429.5	0.3	3.2	7.1	16.2

TABLE X.

## REDUCTION BY MIXTURES OF SUCROSE AND MALTOSE.

Maltose. Mg.	Sucrose in Mg.					
	0.	50.	100.	200.	500.	1000.
0	0	0	0	0	2.1	6.2 mg. Cu
10	10.0	0	0	0.2	1.3	7.2
50	50.5	0	0.3	0.5	3.0	7.9
100	100.8	0	0.6	1.2	3.5	9.9
150	151.5	0	0.5	0.8	3.5	10.6
200	202.0	0	0.6	1.2	4.0	11.1
250	252.5	0	0.5	2.6	4.9	11.0
300	302.6	1.2	1.2	3.6	6.0	11.3
350	353.4	0.8	1.5	5.3	6.1	11.7



It is apparent that the reducing action of sucrose in the presence of dextrose is negligible at concentrations below 400 mg. The greater the proportion of dextrose, the less the action of sucrose; that is, the reducing action of sucrose upon Fehling solution is proportional to concentration of sucrose and amount of copper left unreduced. If enough dextrose is present to precipitate nearly all of the copper in Fehling solution, reduction due to sucrose is slight.

Upon examination of the reducing values of sucrose and dextrose, it appears that for certain concentrations of the two sugars, total reduction is the sum of the two; while at certain concentrations, it is less. Past a certain point, the phenomenon reverses, and dextrose instead of acting as a protector, actually accelerates the decomposition of sucrose. This change in reduction of sucrose decreases however with increasing amounts of dextrose. The decrease in reduction at certain points indicates probably the formation of complex copper sodium sucrates, the dissociation constants of which decrease in the presence of increasing concentrations of the sugar, and this diminishes the alkalinity and concentration of ionizable copper of the reagent. It is obvious therefore, that reduction by sucrose is not entirely a matter of hydrolysis of its molecule, but is a direct function of the molecule itself.

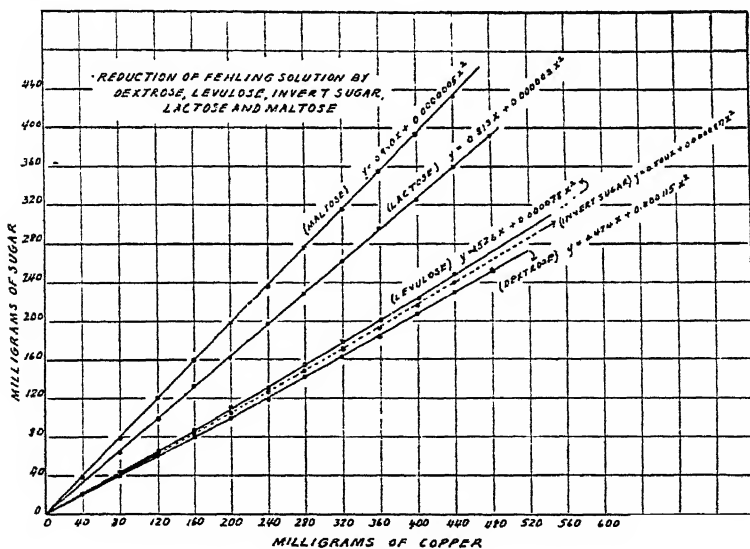


Fig. 7.

Table VII shows that the action of sucrose on levulose is negligible at concentrations below 300 mg. Levulose has an accelerating action upon the decomposition of sucrose, this action being greatest between 40

and 160 mg. of levulose, while in the presence of more than 160 mg. of levulose this phenomenon is not manifested, and as in the case of dextrose, when sufficient reducing sugar is present to precipitate the greater part of the copper, the reducing action of sucrose decreases.

These tables bring out certain effects of the various reducing sugars in the presence of sucrose which are difficult to interpret. The presence of as much as 400 mg. of sucrose does not affect the accuracy of determination of dextrose, while in the case of levulose the presence of 400 mg. of sucrose will cause no appreciable error provided 120 mg. or more of levulose is present. When less than this amount of levulose is present, then not more than 200 mg. of sucrose is permissible for accurate results. A protective action of invert sugar when present in large amounts is shown when mixed with 500 mg. of sucrose, and although this fails to a certain extent when from 1 to 2 g. of sucrose is present, yet the total reduction of the mixture of sugars is less than that of both taken separately.

Maltose and lactose show the odd effect of catalyzing the reduction by sucrose when this sugar is mixed with them. The action of maltose is more marked than that of lactose. It will be noted that in the presence of lactose, not more than 200 mg. of sucrose may be present if the true reducing power of the lactose is desired, and with maltose the amount of sucrose present must not exceed 100 mg. for analyses of high degree of accuracy.

### Preparation of Proposed Modification of Fehling Solution.

1. **Copper Sulfate Solution.**—The crystals of c. p. copper sulfate were washed free from dust, etc., with distilled water and dissolved in hot water to make a saturated solution and filtered. The copper was determined electrolytically and the solution diluted so that 25 cc. of it contained 525 mg. of copper or 41.2 g. of cupric sulfate pentahydrate in 500 cc. of the solution.

2. **Alkaline Tartrate Solution.**—*Sodium hydroxide.* A saturated solution was prepared from sodium hydroxide (purified by alcohol) and let stand for several days until the insoluble carbonates and other impurities had settled out. The clear solution was siphoned off and its alkalinity established by titration with standard acid.

*Crystallized Rochelle salt*, 173 g. (highest purity), was dissolved in water in a 500-cc. graduated flask and the calculated amount of sodium hydroxide solution added, so that 500 cc. of this alkaline tartrate solution contained exactly 65 g. of sodium hydroxide.

It is absolutely necessary that sodium hydroxide for the alkaline tartrate solution should be prepared as described above, because purity

of the reagent and exact concentration of the alkali in Fehling solution has such a decided influence on the oxidizing power of the reagent. Weighing of sodium hydroxide sticks is not recommended.

### General Procedure.

Measure accurately 25 cc. each of the copper sulfate and alkaline tartrate solutions into a 400 cc. Pyrex or Bohemian glass beaker, the diameter of which is about 9 cm. Add 50 cc. of sugar<sup>36</sup> solution making a total volume of 100 cc. Cover the beaker with a watch glass and place the beaker in a water-bath which is maintained at 80°. After exactly 30 minutes' digestion, filter the cuprous oxide by suction through a mat of asbestos in a Gooch crucible. Wash the precipitate in the usual manner and determine the copper by one of the methods discussed at the end of this paper. From the weight of copper or cuprous oxide obtained, find the corresponding weight of reducing sugar from Table XIII or calculate it by means of the equations given below.

### Sugar Table.

Figures in the sugar table were calculated from the equation  $y = a + bx + cx^2$ , by method of least squares,<sup>37</sup> where  $y$  = mg. of sugar and  $x$  = mg. of copper.

$$b = \frac{\Sigma (x^4) \Sigma (xy) - \Sigma (x^3) \Sigma (x^2y)}{\Sigma (x^2) \Sigma (x^4) - [\Sigma (x^3)]^2}$$

$$c = \frac{\Sigma (x^2) \Sigma (x^2y) - \Sigma (x^3) \Sigma (xy)}{\Sigma (x^2) \Sigma (x^4) - [\Sigma (x^3)]^2}$$

Dextrose.....	$y = 0.474x + 0.000115x^2$
Levulose.....	$y = 0.526x + 0.000078x^2$
Lactose.....	$y = 0.813x + 0.000003x^2$
Maltose.....	$y = 0.990x + 0.0000005x^2$
Invert Sugar...	$y = 0.504x + 0.0000870x^2$

<sup>36</sup> Weights of the sugars to be taken for analysis. For dextrose, levulose and invert sugar, take 50 to 150 mg; for lactose and maltose, take 100 to 300 mg. These weights of sugars will reduce about 100 to 350 mg. of copper. In the presence of sucrose, the weight of sample to be taken for analysis can be judged by a preliminary test. In mixtures of sucrose and dextrose up to 400 mg. of sucrose will not influence the accuracy of the determination of dextrose. For mixtures of sucrose and levulose (or invert sugar) not more than 200 mg. of sucrose may be present, unless more than 160 mg. of reducing sugar is present, in which case as much as 400 mg. of sucrose will not affect the result. With sucrose-lactose mixtures the maximol permissible amount of sucrose is 200 mg. and 100 mg. in sucrose-maltose mixtures. In any case, where the composition of the sample is unknown, there will be no danger of error due to the presence of sucrose, if not more than 100 mg. of sample is taken. This allows for the possible presence of maltose.

Mellor, "Higher Mathematics for Students of Physics and chemistry," Longmans, Green and Co., 1916, p. 329.

TABLE XI.

Table for Calculating Dextrose, Levulose, Invert Sugar, Lactose, and Maltose.

Copper. (Cu).	Cuprous oxide (Cu <sub>2</sub> O).	Dextrose. (d-glucose).	Levulose (d-fructose).	Invert sugar.	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> .	Lactose. C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> .H <sub>2</sub> O.	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> .	Maltose. C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> .H <sub>2</sub> O
10	11.1	4.8	5.3	5.0	7.7	8.1	9.4	9.9
20	22.5	9.5	10.5	10.1	15.5	16.3	18.8	19.8
30	33.8	14.3	15.8	15.2	23.2	24.4	28.2	29.7
40	45.0	19.1	21.2	20.3	30.9	32.5	37.6	39.6
50	56.3	24.0	26.5	25.4	38.7	40.7	47.0	49.5
60	67.6	28.9	31.9	30.6	46.4	48.8	56.4	59.4
70	78.8	33.7	37.2	35.7	54.0	56.9	65.8	69.3
80	90.1	38.7	42.6	40.9	61.7	65.0	75.2	79.2
90	101.3	43.6	48.0	46.1	69.5	73.2	84.6	89.1
100	112.6	48.6	53.4	51.3	77.2	81.3	94.0	99.0
110	123.8	53.5	58.8	56.5	85.0	89.5	103.4	108.9
120	135.1	58.5	64.3	61.8	92.7	97.0	112.8	118.8
130	146.4	63.6	70.7	67.0	100.4	105.7	122.2	128.7
140	157.6	68.6	75.2	72.3	108.2	113.9	131.6	138.6
150	168.9	73.7	80.7	77.6	116.0	122.0	141.0	148.5
160	180.1	78.8	86.2	82.9	123.7	130.1	150.4	158.4
170	191.4	83.9	91.7	88.3	131.4	138.3	159.8	168.3
180	202.6	89.1	97.2	93.7	139.1	146.4	169.2	178.2
190	213.9	94.2	102.8	99.1	146.9	154.6	178.8	188.1
200	225.2	99.4	108.4	104.4	154.6	162.7	188.2	198.0
210	236.4	104.6	114.0	109.8	162.3	170.9	197.6	207.9
220	247.7	109.9	119.6	115.2	170.0	179.0	207.0	217.8
230	258.9	115.1	125.2	120.6	177.8	187.2	216.4	227.7
240	270.2	120.4	130.8	126.1	185.5	195.3	225.8	237.6
250	281.5	125.7	136.4	131.6	193.2	203.4	235.2	247.5
260	292.7	131.0	142.1	137.1	201.0	211.6	244.6	257.4
270	304.0	136.4	147.8	142.6	208.8	219.8	254.0	267.3
280	315.2	141.7	153.5	148.2	216.5	227.9	263.4	277.2
290	326.5	147.1	159.2	153.7	224.2	236.0	272.8	287.1
300	337.8	152.6	165.0	159.3	232.0	244.2	282.2	297.0
310	349.0	158.0	170.7	164.9	239.7	252.3	291.6	306.9
320	360.3	163.5	176.5	170.5	247.5	260.5	301.0	316.8
330	371.5	168.9	182.3	176.1	255.3	268.7	310.4	326.7
340	382.8	174.5	188.1	181.8	263.0	276.8	319.8	336.6
350	394.0	180.0	193.9	187.4	270.7	285.0	329.2	346.5
360	405.3	185.5	199.7	193.1	278.4	293.1	338.6	356.4
370	416.6	191.1	205.5	198.8	286.2	301.3	348.0	366.3
380	427.8	196.7	211.4	204.5	293.9	309.4	357.4	376.2
390	439.1	202.3	217.3	210.2	301.6	317.5	366.8	386.1
400	450.3	208.0	223.2	216.0	309.4	325.7	376.2	396.0
410	461.6	213.7	229.1	221.8	317.1	333.8	385.6	405.9
420	472.9	219.4	235.0	227.6	324.9	342.0	395.0	415.8
430	484.1	225.1	240.9	233.4	332.6	350.1	404.4	425.7
440	495.4	230.8	246.9	239.2	340.4	358.3	413.8	435.6
450	506.6	236.6	252.9	245.0	348.1	366.4	423.2	445.5
460	517.9	242.4	258.9	250.9	355.9	374.6	432.6	455.4
470	529.1	248.1	264.9	256.8	363.6	382.7	442.0	465.3
480	540.4	250.8	270.9	262.7	371.3	390.9	451.4	475.2

TABLE XII.—REDUCING RATIOS.

Showing the Reducing Ratios of Levulose, Invert Sugar, Lactose and Maltose by the New Method.

Copper. Mg.	Dextrose. Levulose.	Dextrose. Invert sugar.	Dextrose. Lactose.	Dextrose. Lactose hydrate.	Dextrose. Maltose.	Dextrose. Maltose hydrate.
50	0.905	0.945	0.620	0.589	0.510	0.489
100	0.906	0.947	0.629	0.598	0.517	0.491
150	0.913	0.950	0.635	0.604	0.522	0.496
200	0.917	0.952	0.642	0.611	0.528	0.502
250	0.921	0.955	0.650	0.618	0.534	0.508
300	0.924	0.957	0.657	0.624	0.540	0.513
350	0.928	0.960	0.665	0.631	0.546	0.519
400	0.932	0.963	0.672	0.638	0.552	0.525
450	0.935	0.965	0.679	0.645	0.559	0.531
	0.920	0.955	0.651	0.618	0.534	0.508

These ratios were calculated from the sugar values corresponding to the several weights of copper in Table XI. The ratios for levulose and invert sugar are approximately equal to those obtained by Browne<sup>38</sup> using Allihn's method. The ratios for lactose and maltose are lower than those obtained by others.<sup>39,40</sup>

### Determination of Reduced Copper.

Three different methods were used (1) direct weighing of cuprous oxide, (2) E. C. Kendall's<sup>28</sup> modified iodide method, and (3) H. T. Beans and J. W. Stillman's<sup>24</sup> electrolytic method. For economy of space our extensive comparative tests of these three methods are omitted.

While the direct weighing of cuprous oxide is the quickest, it is liable to inaccuracy when solutions other than of pure sugars are used due to contamination of the precipitate with mineral and organic impurities. The extent of this error has been shown by Sherwood and Wiley.<sup>41</sup>

Kendall's modified iodide method is rapid but has the disadvantage of a poor end-point.

The reduced copper values given in the main sugar table No. XI and in most of the other tables in this paper were determined by the Beans and Stillman electrolytic method. This new electrolytic method is very rapid, and since the technique is at present available only in the original dissertation, it seems desirable to abstract it in brief.

**Electrolytic Method.**—The cuprous oxide is dissolved with 10 to 20 cc. of 16 *M* nitric acid, and the solution diluted to about 200 cc. with distilled water. Ten cc. of a 3% hydrogen peroxide is added. The solution is then electrolyzed at room temperature (18° to 25°) with a current of 1 ampere and an e. m. f. of from 2.5 to 3.5 volts. A weighed 50-mesh, platinum-gauze cathode and a platinum-wire spiral anode serve as electrodes. A mechanical stirrer is used so that there will be rapid agitation of the

<sup>38</sup> Browne, *op. cit.*, 1912, p. 421; *THIS JOURNAL*, 28, 436 (1906).

<sup>39</sup> Browne, *op. cit.*, p. 421.

<sup>40</sup> Sherman, "Organic Analysis," Macmillan and Co., 1918, p. 73.

<sup>41</sup> Sherwood and Wiley, *Bur. Chemistry, Bull.* 105, 120 (1907).

electrolyte. During the electrolysis a 3% solution of hydrogen peroxide is constantly dropped into the electrolyte. When the solution has become colorless, the sides of the beaker and the cover glasses are washed with distilled water, thus raising the level of the electrolyte and exposing a new surface of the platinum cathode. The process is continued until this new surface shows no deposit of copper. When the electrolysis is complete, the cathode is quickly lifted from the solution without interrupting the current and placed in a beaker containing distilled water. The electrode with its deposit of copper is washed with 95% alcohol, dried in an oven at 100° for a minute or two, then cooled in a desiccator, and weighed.

### Accuracy of Proposed New Method for Determination of Reducing Sugars.

Under the conditions for reduction, a series of experiments with dextrose and lactose was performed to study the degree of accuracy of the method.

TABLE XIII.

Reduction of Fehling Solution by Reducing Sugars.

Wt. of sugar in mg.	Reduction in mg. of copper.				
Dextrose.	(1).	(2).	(3).	(4).	(5).
20	42.2	42.0	42.6	42.3	42.3
50	102.3	102.4	102.4	102.9	102.6
100	201.2	201.2	201.0	201.2	201.1
150	295.2	...	295.1	295.4	...
200	385.1	385.6	385.0	385.4	384.8
250	472.7	...	473.2	472.6	472.7
Lactose.	(1).	(2).	(3).		
10	10.7	11.3	10.6		
50	61.2	61.3	61.6		
100	122.5	122.1	123.0		
150	184.0	184.2	184.4		
200	245.7	246.6	245.9		

From the above Table, the mean error of the mean computed from the least square equation,  $m = \pm \sqrt{\frac{\sum d^2}{n(n-1)}}$  was calculated, where,  $m$  is the mean error of the mean;  $d$  the deviation from the mean, and  $n$  the number of determinations.

The mean error of the mean for dextrose and lactose under these conditions appears to be  $\pm 0.08$  and  $\pm 0.17$  mg. of copper respectively. The percentage error is approximately  $\pm 0.12\%$ . Besides the "mean error," in the mean there may be constant errors which arise either during the preparation of the solution and weighing of samples, etc. These results show that the method is highly accurate compared with the current methods of sugar analysis, and the slight differences may be called negligible.

TABLE XIV.  
The Effect of Temperature Deviations.

Wt. of sugar in mg.	Temperature. °C.				
	78.	79.	80.	81.	82.
Dextrose.					
50	102.1	102.0	102.5	102.3	103.7
100	201.5	201.9	202.2	202.7	203.4
200	385.7	385.9	386.2	386.7	387.2
Lactose.					
100	120.7	121.6	122.2	123.5	124.5
200	244.3	245.0	245.6	246.6	247.2
300	366.8	367.3	368.2	368.7	370.2

The mean error of the mean as calculated from these figures appears to be  $\pm 0.23$  and  $\pm 0.44$  mg. of copper for dextrose and lactose respectively for every degree of temperature change around  $80^\circ$ , and  $\pm 0.50$  and  $\pm 0.94$  mg. of copper for dextrose and lactose for every  $2^\circ$ . This error is approximately equal to  $\pm 0.3\%$  for  $\pm 1^\circ$  and  $\pm 0.65\%$  for  $\pm 2^\circ$  around  $80^\circ$ . The greater difference in reducing value for lactose may be ascribed to its greater susceptibility to decomposition by Fehling solution. Experiments show that the temperature can be regulated with a set of burners, and results indicate that the error introduced by fluctuations in temperature of  $\pm 1^\circ$  does not materially affect the degree of accuracy required for most purposes. For high accuracy an automatically temperature controlled bath should be used.

### Summary.

The various sources of error in current methods for using Fehling solution have been discussed.

The interrelationship of temperature,  $60^\circ$  to  $110^\circ$ , and time of heating, 10 minutes to 2 hours, to determine the best time and optimum temperature for reduction has been investigated.

Fehling reagent has been studied from the standpoint of nature and concentration of alkali, concentration of copper sulfate and Rochelle salt to find the maximum and minimum concentrations of these constituents necessary to give the greatest yield of cuprous oxide and to ensure the formation of the complex cupric tartrate ion.

Auto-reduction of Fehling solution at different times and degrees of heating has been measured, revealing those conditions under which absolutely no "blank" reduction is obtained.

Conditions affecting the physical properties of the precipitated cuprous oxide, the photosensitiveness and keeping quality of Fehling solution have been recorded.

A study of surface oxidation involving different methods of heating and receptacles of various sizes has been carried out in order to determine

the amount of copper lost due to surface oxidation and how to avoid it. The catalytic effect of the walls of the container has been demonstrated.

A procedure for the proposed method with comparison of results for the determination of the reduced copper has been described, including a discussion of the degree of accuracy of the new method.

The reducing action of sucrose on Fehling solution, alone and when mixed with different proportions of reducing sugars, has been investigated with the view of elimination of the use of empirical formulas and factors for calculation of errors involved.

The new method is designed for use in the analysis of saccharine materials containing sucrose, dextrose, levulose, invert sugar, lactose and maltose. It is not claimed that this method can be used for the accurate quantitative determination of 0.1% or less of invert sugar in approximately pure sucrose.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NATIONAL BISCUIT COMPANY,  
No. 1.]

## VISCOSITY OF GELATIN SOLUTIONS.

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Received March 7, 1921.

Owing to the divergence of results and conclusions arrived at regarding the various physical properties of gelatin solutions an investigation of the effects of different physical and chemical treatments of such solutions has been undertaken by this laboratory.

In this paper the investigation of the viscosity of gelatin solutions is described. Detailed results of the effects on viscosity of (1) method of effecting solution, (2) aging of solution, (3) concentration of hydrogen ion, (4) concentration of gelatin, (5) hydrolysis of gelatin are given for three different types of gelatins. Finally, a method is given whereby the viscosity of a gelatin may be determined with an accuracy well within 0.5%.

Previous work has shown that viscosity is affected by the age of the solution, concentration of the gelatin, the temperature employed for effecting solution and by the character of the gelatin. With the exception of the first two factors very few, if any, results of a definite nature have been published. Much work has been done on the effects of various salts, but Loeb<sup>1</sup> has shown the fallacy of the "Hofmeister Series" and has furnished adequate chemical data in explanation of such salt effects.

<sup>1</sup> Loeb, *J. Gen. Physiol.*, [III] 1, 85 (1920).



Gelatins are of at least three kinds, depending upon the method of manufacture. No. 1 is obtained by extracting ground bones with water, leaving the mineral matter behind. No. 2 is obtained as a residue from the same source by dissolving the mineral matter in dilute acid; No. 3 is obtained by extracting hides with water, concentrating, grinding and drying. Samples of all three kinds were used in this investigation. The various grades of these different kinds depend upon the temperature and length of time required for solution. The last fractions dissolved having been subjected to the water at a higher temperature for a greater length of time furnish the weaker jells and are probably more hydrolyzed as well as more affected by any bacterial action that may have been proceeding during the manufacture. Table I will show as nearly as is possible, at the present time, the characteristics of the three gelatins investigated.

TABLE I.

Gelatin	Moisture.	Ash.	$p_H$ in 1% Sol.	Jell strength.	Bacteria per g.
1	8.93	2.39	5.5	59	22,000
2	11.25	.84	4.1	430	200
3	5.25	1.03	4.0	800	100

The jell strengths of these gelatins were determined by a more or less arbitrary procedure. A solution of 30 g. of gelatin in 180 cc. of water was heated to 60° and placed in a standard glass of 250 cc. capacity. This was cooled to 21°  $\pm$  0.1° and maintained at this temperature for 16 hours. Then the number of grams required to force a plunger a certain distance into the surface of the gelatin was determined by a method which will be described in detail in a later paper.

The  $p_H$  values of the dry gelatin were determined by applying indicators directly. This gave an accuracy of 0.2 or 0.3 in the  $p_H$  value. In determining the hydrogen-ion concentration of solutions, comparison with the color of the indicators in buffer solutions of known hydrogen-ion concentration was necessary. By employing buffer solutions and indicators as described by Clark and Lubs<sup>2</sup> an accuracy of less than 0.2 was readily attained except at a  $p_H$  of 4 to 4.5 where the solution absorbs so much of the red rays as to render color comparison with buffer solutions difficult. 1% solutions of all gelatins gave the same hydrogen-ion concentration as did the dry gelatins.

### Method of Effecting Solutions.

Preliminary determinations of the variation of viscosity of solutions of a given gelatin with change in hydrogen-ion concentration gave erratic results. From these preliminary data we were convinced however of two things. First there is a distinct effect of hydrogen-ion concentration on viscosity and second the dissolving temperature has an effect on the nature of the solution. These first results plainly showed that the alkaline solutions were more difficult to effect than the acid ones. For concordant viscosity results on solutions of the same gelatin the dissolving temperature of the alkaline solutions must be greater than of the acid solutions. Upon a more complete investigation of the effect of the temperature employed for bringing about solution it was found that all solutions brought to a temperature of 75° gave concordant viscosity results. At temperatures somewhat lower than this the results on different portions of the same so-

<sup>2</sup> Clark and Lubs, *J. Wash. Acad. Sci.*, 6, 483 (1916); *J. Biol. Chem.*, 25, 479 (1916).

lution did not agree. At higher temperatures there was a rather rapid lowering in viscosity. At the boiling temperature this decrease in viscosity was extremely rapid as will be noted in the results given in Table II and plotted in Fig. 1. These results, which are quite in accord with the previous work of Von Schroeder,<sup>3</sup> show that a very few minutes' boiling reduced the viscosity of a high grade gelatin to that of a low grade one and entirely destroyed its tendency to increase in viscosity with aging of solution. Excessive temperatures should therefore be avoided in

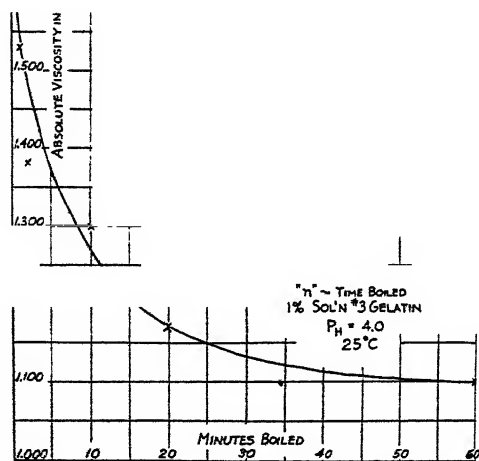


Fig. 1.

effecting solution. Since a temperature of 75° served to produce solutions whose viscosity could be accurately duplicated over the entire range of hydrogen-ion concentration and lower temperatures did not, this was selected as the standard. At this temperature the hydrolysis of the gelatin with its consequent lowering of viscosity was very slow except in certain cases detailed later.

From this preliminary work the following standard procedure was adopted. Ordinary distilled water ( $p_H$  value about 5.6) is made acid or basic by the addition of such quantity of 0.2 *M* hydrochloric acid or 0.2 *M* sodium hydroxide as will bring the resulting gelatin solutions to the required hydrogen-ion concentration. The gelatin is added to such

<sup>3</sup> Von Schroeder, *Z. physik. Chem.*, **45**, 75<sup>v</sup> (1903).

TABLE II.

Viscosity of Boiled Solutions of No. 3 Gelatin. Concentration 1% at 25°;  $p_H$  4.0.

Duration of boiling, min.	Age of sol. Min.	C.p. Absolute viscosity.
0	26	1.681
	39	1.769
	49	1.797
	60	1.816
	62	1.844
	91	1.960
	98	1.976
	114	2.056
	118	2.062
1.0	65	1.482
	76	1.503
	91	1.518
2.0	84	1.371
10.0	72	1.304
	85	1.298
	97	1.306
	109	1.303
20.0	99	1.170
60.0	113	1.100

quantity of this solution as will give the required weight concentration. The age of the solution is reckoned from the time the gelatin is placed in contact with the water. As soon as the gelatin is added the flask is placed on the hot plate and brought to a temperature of 75° in 20 minutes, and stirred constantly. The solution is then filtered and placed in the thermostat at 25°  $\pm$  0.02°. When the solution registers this temperature 5 cc. is pipetted into an Ostwald viscometer and the whole immersed in the thermostat for at least 10 minutes. The solution is then drawn into the bulb of the viscometer and the run made while in the thermostat, timing the flow with a stopwatch. Three or four runs were made on each solution, using different viscometers of water equivalents of 73.8, 75.0, 78.4 and 75.8 seconds respectively. Specific gravity determinations were made by means of a pycnometer. The viscosity coefficient was calculated according to the customary formula,

$$\eta \text{ (Gelatin)} = \eta \text{ (Water)} \times \frac{(\text{Sec. gel. sol.}) \times (\text{Sp. gr. gel. sol.})}{(\text{Sec. water}) \times (\text{Sp. gr. water})}$$

$\eta$  for water being taken as 0.008937 absolute units or 0.8937 c. p. as given by Bingham.<sup>4</sup> Curiously enough no appreciable difference could be detected in the density of the solutions of the different grades of gelatin from the poorest to the best. The variation of the densities with different

<sup>4</sup> Bingham. Bur. Standards, *Bull.* 298, 74 (1917).

values of the concentration of the hydrogen ion was negligible in its effect on viscosity results.

In all our computations the density of the 1% gelatin solutions at 25° was taken as 1.0000. Actual variations were encountered from 1.00008 to 0.99988. The densities of gelatin solutions will be discussed in detail in a later paper.

The instruments were cleaned after each run by sucking through hot tap water and then distilled water by means of the filter pump. They were then placed in an air-oven and heated and air drawn through them while they were still warm. It is extremely important that the viscometer be absolutely dry when the gelatin solution is drawn into the side tube, as otherwise bubbles will be formed and correct results cannot be obtained. The  $p_H$  values between 2 and 9 were determined colorimetrically with the indicators and buffers of Clark and Lubs.<sup>3</sup> Other values were determined with the hydrogen electrode, using the condenser method described by Beans and Oakes.<sup>5</sup> The hydrogen electrode also served to check colorimetric determinations.

This procedure was found to give such satisfactory results that it was followed for all the viscosity determinations. It was found that under identical conditions the viscosity of solutions of any gelatin could be duplicated at will within the accuracy of the stopwatch. This gave an accuracy in the absolute viscosity values of  $\pm 5$  in the fifth decimal place, or in the third decimal place where viscosity is given in c. p. or an error of about  $\pm 0.5\%$  at the most.

### Effect of Age of Solution on Viscosity.

Attention has been directed to the fact that gelatin solutions increase in viscosity for a period of time, reach a maximum and then diminish in viscosity. This phenomenon has been investigated for all three kinds of gelatin. It has been found that the maximum viscosity is attained in about 24 hours. Solutions of the higher grade gelatins may then still continue to increase slowly in viscosity. The low grade gelatins show a fairly rapid decrease especially where the  $p_H$  value of the solution is between about 5 and 8. It was noted that in every case where the viscosity began to decrease the solution smelled putrid; it was the gelatin of the highest bacterial content that decreased most rapidly; the decrease was accelerated by conditions favoring bacterial growth.

Table III shows the effect of age on the lowest grade of gelatin which also contains the greatest number of bacteria per gram. In Table IV will be found data covering the effect of age on solutions of the highest grade gelatin over periods of 1 and 2 hours.

<sup>5</sup> Beans and Oakes, *THIS JOURNAL*, 42, 2116 (1920).

TABLE III.

Effect of Age of Solution on the Viscosity of 1% Solutions of Gelatin No. 1 at  $p_H$  5.0.

Age of solution.		C. p. Absolute viscosity.
Hrs.	Min.	
0	43	1.062
0	95	1.058
0	108	1.060
25	43	1.126
66	35	1.096
90	48	1.075

The viscosities of solutions of various concentrations of all three gelatins were investigated over a range of  $p_H$  value 1.5 to 12.9. In order to show in detail the method of procedure the complete results on 1% solutions of Gelatin No. 3 are given in Table IV. The last column gives the increases in viscosity during the second hour multiplied by 100 to avoid the use of small fractions. Similarly 0.5% and 0.25% solutions of this same gelatin were investigated.

TABLE IV.

Viscosities of 1% Solutions of No. 3 Gelatin at 25°.

Cc. of 0.2M HCl and NaOH contained in 200 cc of solution		$p_H$	Age of solution in min	C.p. absolute viscosity	$10^2 \frac{\Delta\eta}{\Delta T}$ For 2nd hour
HCl.	NaOH				
6.0	0	3.0	65	1.990	10.5
			86	2.020	
			114	2.067	
			26	1.681	
0	0	4.0	39	1.769	24.9
			49	1.797	
			60	1.816	
			62	1.845	
			91	1.960	
			98	1.976	
			114	2.056	
			118	2.062	
	1.0	4.6	68	1.788	29.6
			91	1.927	
			110	2.005	
			127	2.081	
	2.0	4.8	70	1.923	21.6
			87	1.960	
			108	2.074	
			127	2.126	
	3.0	4.9	74	1.724	39.0
			90	1.793	
			107	1.924	
			120	2.032	

TABLE IV.—(Continued).

Cc. of 0.2 M HCl and NaOH contained in 200 cc. of solution.		$p_H$	Age of solution in min.	C. p. absolute viscosity.	$10^3 \frac{\Delta\eta}{\Delta T}$ For 2nd hour.
HCl.	NaOH.				
4.0	5.2		67	1.756	45.6
			89	1.931	
			101	1.985	
			117	2.143	
			159	1.634	
5.0	6.3		72	1.813	73.5
			161	2.840	
			177	3.023	
			63	1.592	
			93	1.987	
5.5	7.1		111	2.250	74.2
			136	2.497	
			67	1.831	
			90	2.151	
			124	2.701	
6.5	8.4		170	3.460	87.1
			66	1.443	
			91	1.489	
			127	1.609	
			157	1.648	
10.0	10.0				16.3

In Fig. 2 the viscosity values for all three concentrations are plotted for  $p_H$  4.0, while in Fig. 3 corresponding values for  $p_H$  6.5 are plotted. Reference to these curves (Figs. 2 and 3) shows that the rate of increase

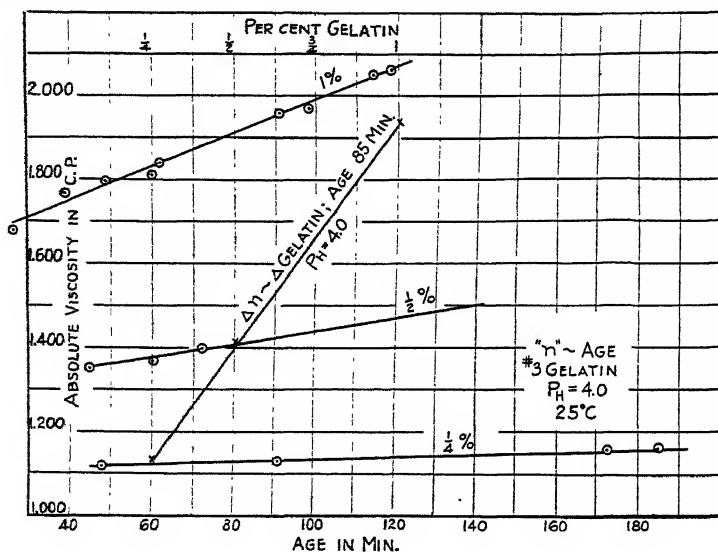


Fig. 2.

in viscosity with aging of solution differs at different  $p_H$  values. In Fig. 4 the viscosity-age of solution results are plotted for several different  $p_H$  values for 1% solutions of No. 3 gelatin. From this figure it is seen that the slopes of the curves increase with concentration of hydroxyl ion until a maximum is reached when the slope drops rapidly to a new low level. In order to represent this more clearly the values of  $10^3 \frac{\Delta \eta}{\Delta t}$  for the second hour of age of solution have been plotted in Fig. 5. In this figure the corresponding values of No. 2 gelatin are also given, No. 1 gelatin gave such small values as could not be plotted on the same scale with No. 2 and No. 3. From Fig. 5 it is seen that the viscosity is increasing most rapidly around a  $p_H$  value of 8. At a concentration of hydroxyl ion greater than  $p_H = 9$  there may even be a decrease in viscosity. This effect is taken up later under hydrolysis of gelatin.

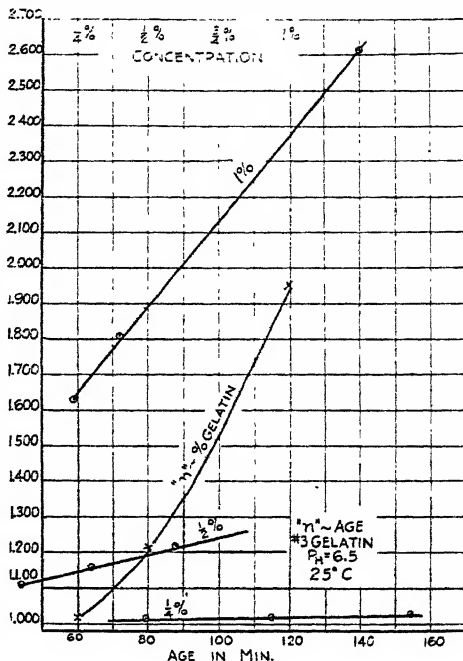


Fig. 3.

We may then conclude from the results described above that a solution

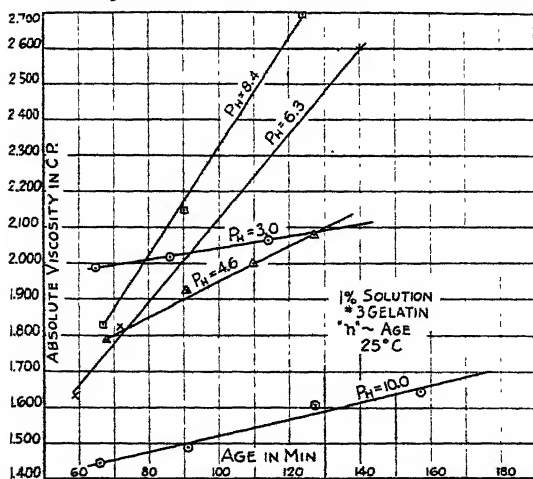


Fig. 4.

of gelatin of  $p_H$  value less than 9 increases in viscosity with increase in age, reaching a maximum in about 24 hours. A decrease in viscosity after the maximum is reached indicates bacterial decomposition. The increase in viscosity with age varies directly with the hydroxyl-ion concentration until a maximum is reached at  $p_H$  8 to 8.5. At greater hydroxyl-ion concentration the in-

crease diminishes rapidly and actually becomes a minus quantity at  $p_H$  values somewhat greater than 9. In the case of pure, strong, slightly hydrolyzed gelatin the increase is very rapid. Very low grade gelatins show but slight increase in viscosity with age of solution.

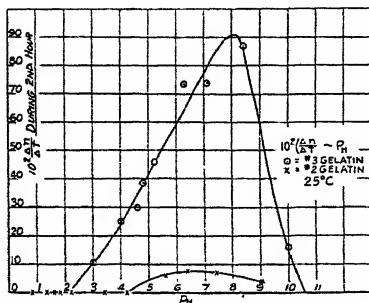


Fig. 5.

#### Effect of Concentration of Gelatin on Viscosity.

In Figs. 2 and 3 the viscosity-concentration values of No. 3 gelatin are plotted for  $p_H$  4.0 and 6.5 respectively. In Fig. 8 the corresponding values for No. 1 gelatin are plotted for  $p_H$  3.6 and 5.0. In the case of No. 1 the concentrations were carried to 3%. With No. 3, solutions of greater concentration than 1% jellied too rapidly to give reliable results. For low concentrations of fairly acid solutions the viscosity is approximately a linear function of the concentration.

On the alkaline side of the iso-electric point ( $p_H$  4.7) the viscosity increases so rapidly with increasing concentration that it does not even approximate a linear function of the concentration. It is quite evident from the above that neither Einstein's<sup>6</sup> formula for the viscosity of a colloid solution nor any modification so far proposed for it can be used to compute the viscosity of gelatin solutions at different concentrations. Viscosity-concentration formulas for gelatin solutions would require an entirely different set of constants for each gelatin, each value of the hydrogen-ion concentration, each age of solution, and in addition the method of effecting solution would have to be defined.

#### Effect of Concentration of Hydrogen Ion.

Since at a temperature of 25° gelatin solutions increase in viscosity with age it is obvious that viscosity values are worthless unless the age of solution is stated. Accordingly in all our work a number of determinations were made on each solution. From these values a graph was constructed from which the viscosity of the solution at any particular age

<sup>6</sup> Einstein, *Ann. physik.*, 19, 289 (1906).



could be determined. Selecting the values for an age of solution of 85 minutes the viscosity- $p_H$  values for 0.25 to 0.5% and 1% solution of No. 3 gelatin were plotted in Fig. 6. In Fig. 7 the corresponding values for 1% solutions of No. 1 and No. 2 are plotted with the values for 0.25% solutions of No. 3 repeated for comparison. 1% solutions of No. 3 gelatin are increasing in viscosity so rapidly that the gelation factor has entirely masked the effect of hydrogen-ion concentration. The other curves show a distinct maximum at  $p_H$  3.0 to 3.5 when the viscosity is taken at an age of solution of 85 minutes and  $25^\circ$ . On the alkaline side of the iso-electric point the corresponding viscosities plot a straight line until such a concentration of hydroxyl ion is reached as will catalyze the hydrolysis of the gelatin as described later. On the acid side the curves are essentially the same as described by Loeb.<sup>1</sup> On the alkaline side the type of curve is quite different since Loeb records a maximum at  $p_H$  11 approximately. Since Loeb<sup>7</sup> used an entirely different procedure undoubtedly a difference in the ages of the solutions accounts for the difference in the types of the curves. The maximum in the curve at  $p_H$  3 to 3.5 is unaccounted for except on the assumption of the formation of a compound at this point, data included in a paper in the course of preparation support this view.

### Effect of Hydrolysis on Viscosity.

The effect of hydrolysis of the gelatin resulting from boiling the solution has been discussed. The abnormal drop in viscosity recorded in Figs. 6 and 7 at  $p_H$  values greater than 9 suggests that we are encountering an

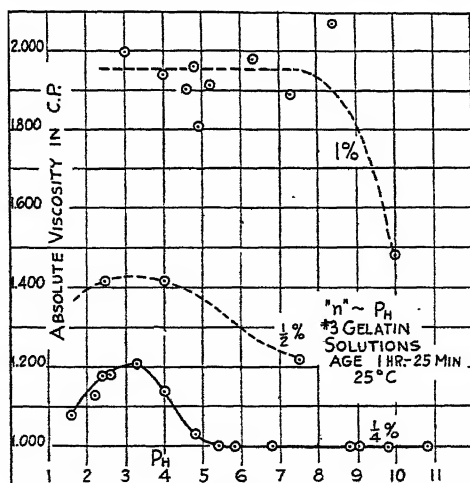


Fig. 6.

<sup>7</sup>This work was done in the summer of 1920, before Loeb's results were published in September (1920).

effect other than that of the alkali combining with the gelatin to form a metal gelatinate. It appeared that the hydroxyl ion at this concentration was catalyzing the hydrolysis of the gelatin to such an extent as to lower the viscosity to the extent indicated in Fig. 7, the actual values being 1.251 at  $p_H$  values 6.4, 7.4, 9, and 1.047 at  $p_H$  12.9.

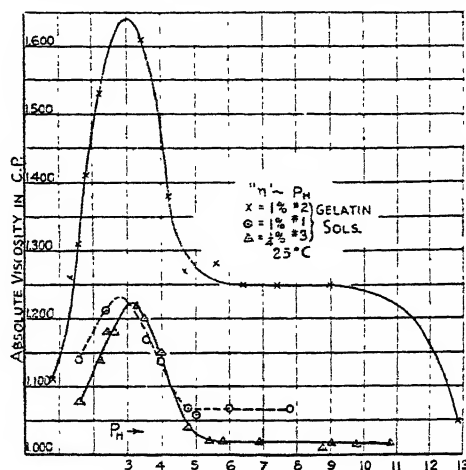


Fig. 7.

In order to test this point 1% solutions of No. 2 gelatin were made up in duplicate. Solution B1 was made up exactly as described heretofore. Two g. of gelatin was dissolved in 200 cc. of 0.2 M sodium hydroxide

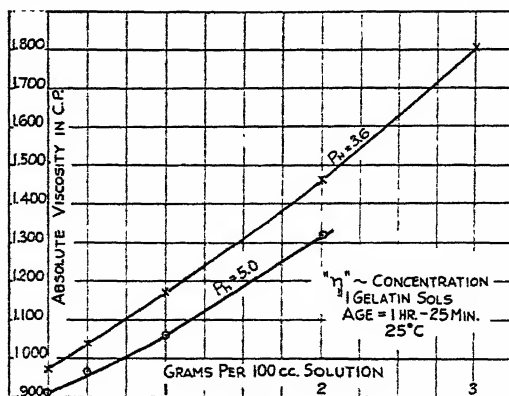


Fig. 8.

solution, heated for 20 minutes, when a temperature of 75° was reached, allowed to cool, filtered and placed in the thermostat. At the same time Solution B2 was prepared as follows. Two g. of the gelatin was added

to 190 cc. of water and the solution accomplished exactly as in the case of Sample B1, the two solutions being carried along together. After B2 was removed from the hot plate and allowed to cool 10 cc. of a solution containing 1.6 g. of sodium hydroxide was added. The  $p_H$  value of these two solutions, B1 and B2 was 12.9. Viscosity of these solutions was found to be as follows.

Age of solution.		C. p. B1 absolute viscosity.	C. p. B2 absolute viscosity.
Hours.	Min.		
1	25	1.009	1.273
5	30	0.987	1.100
22		0.979	1.019
27		0.976	1.007
49		...	0.996

In exactly the same manner the effect of acids on the hydrolysis of gelatin solutions was determined. Solutions A1 and A2 were made up at a  $p_H$  1.4. In the case of A1, 2 g. of gelatin was dissolved in 160 cc. of water to which 40 cc. of 0.2 *M* hydrochloric acid had been added. A2 solution did not have the acid added until after the gelatin had been dissolved and the solution cooled. On these two solutions the following results were obtained.

Age of solution.		C. p. A1 absolute viscosity. $p_H$ 1.4.	C. p. A2 absolute viscosity. $p_H$ 1.4.
Hours	Min.		
1	40	1.379	1.424
22	"	1.449	1.515
28		1.447	1.501

These values indicate that hydrogen ions and hydroxyl ions catalyze the hydrolysis of gelatin. Hydroxyl ion catalyzes this reaction to a very great extent at  $p_H$  values greater than 9. The effect of hydrogen ion up to  $p_H$  1.4 is slight compared to the hydroxyl-ion effect. In order to avoid the hydrolysis effect the acid and the alkali should not be added to the solution until after it has been cooled. The procedure would then be to dissolve the gelatin in pure water and after the solution has cooled add the required amount of alkali or acid to bring the solution of gelatin to the required hydrogen-ion concentration making the total volume such as will give the desired gelatin concentration. This would only be necessary where the hydrogen-ion concentration of the resulting solution was outside the range of  $p_H$  2.5 to 8.

### Summary.

1. Effects on the viscosity of gelatin of (a) method of effecting solution, (b) aging of solution, (c) hydrogen-ion concentration, (d) concentration of gelatin, and (e) hydrolysis of gelatin, have been described for three different kinds of gelatin.

2. A method of determining viscosity of gelatin solutions with a maximum error of 0.5% has been described.

3. Gelatin solutions increase in viscosity with age at different rates depending upon concentration of gelatin, hydrogen-ion concentration, and kind of gelatin.

4. For any given gelatin solution a maximum viscosity is attained at an age of solution of about 24 hours. A decrease in viscosity after the maximum is reached indicates bacterial decomposition.

5. Gelatin solutions show a maximum viscosity at a  $p_H$  3.0 to 3.5 at 25°.

6. The viscosity of gelatin solutions is not a simple function of concentration of gelatin.

7. Both hydrogen and hydroxyl ions catalyze the hydrolysis of gelatin solutions, the latter more rapidly than the former.

8. Excessive temperatures catalyze the hydrolysis of gelatin. Boiling gelatin solutions hydrolyzes them very rapidly.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

## THE COMPRESSIBILITY OF BENZENE, LIQUID AND SOLID.

BY THEODORE W. RICHARDS, EDWARD P. BARTLETT AND JAMES H. HODGES.

Received March 11, 1921.

Very few substances have had their compressibilities determined in both the liquid and the solid state. The comparison of the two different values is of considerable interest in relation to a study of the mechanism of the change of state in any given substance. Accordingly the present paper recounts such a comparison in the case of benzene, for which adequate data were lacking as regards the solid. The results were incidental to other researches, but seem to deserve separate publication.

Of liquid benzene, a careful determination, made in a glass piezometer, has already been described.<sup>1</sup> The object of repeating the determination was primarily to show whether or not the earlier apparatus, which had been used with a variety of substances, was adequate, by comparing a typical result with that yielded by a larger more complete piezometer free from the hysteresis to which glass is subject.

The piezometer used in the present research was the steel instrument already described in full in another previous paper.<sup>2</sup> In the case of liquid benzene, a weighed amount of about 30 cc. of this substance was placed in an inverted steel test-tube immersed under mercury (which filled the piezometer). The steel test-tube diminished the unnecessarily large volume

<sup>1</sup> T. W. Richards and J. W. Shipley, *THIS JOURNAL*, 38, 989 (1916).

<sup>2</sup> T. W. Richards and E. P. Bartlett, *ibid.*, 37, 470 (1915).

of the apparatus and kept the benzene from being entrapped in the washer and screw-thread. During the operation of filling, the utmost care was exercised against the introduction of air. From Amagat's measurement of the compressibility of air<sup>3</sup> 1 cc. at 0° and 1 atmosphere changes in volume by 0.007 cc. between 100 and 500 atmospheres. Since the present method is sensitive to perhaps within 0.0001 cc., the presence of even 0.01 cc. of air should be avoided. Accordingly, after having been thoroughly cleaned and dried, the piezometer was filled with mercury through a funnel tube with a capillary outlet reaching to its bottom. The mercury thus rose quietly in the steel tube, without entrapping air. The iron washer was slipped edgewise under the mercury, and put in position with two glass rods. The piezometer was then ready to receive the tube containing the hydrocarbon. The benzene having been inserted, the cap-piece of the piezometer with the attached capsule, was carefully put in position and held firmly until the nut was screwed into place, when, with a special vise, the nut was tightened as much as possible, using a long lever to complete the closure.

It was by no means so easy to arrange the solid benzene for compression. In the first place, the steel piezometer was prepared as before in every respect for the reception of the tube containing the benzene, since its introduction was a process demanding great celerity, as will be seen.

The hydrocarbon was enclosed in a glass tube of 17.82 cc. capacity, drawn down to a capillary opening. This tube had been filled by placing it in a large test-tube containing the liquid, and by alternately exhausting and admitting pressure. Unfortunately benzene dissolves a considerable amount of air,<sup>4</sup> which separates when the liquid is frozen. Accordingly, when the tube was completely full of benzene, the whole apparatus was immersed in ice water, still keeping it at low pressure. As the liquid froze, the dissolved air was set free. Because, however, the crystals entangled a few bubbles, the benzene was melted and frozen again several times successively, until no further air appeared on freezing. The apparatus was finally warmed to about 23° and the tube removed, wiped, and weighed as quickly as possible on a balance already holding the known approximate weights. Slight warming brought the benzene exactly to the orifice, when the tube was quickly inverted and immediately inserted in the waiting piezometer. The only surface exposed was that in the capillary about a millimeter in diameter, so that evaporation, or solution of air, must have been negligible in the very brief time concerned. The remainder of the closing of the piezometer was conducted just as usual, and so were the details of the application of pressure.

<sup>3</sup> Amagat, *Compt. rend.*, 111, 871 (1890), and 116, 946 (1893).

<sup>4</sup> T. W. Richards, E. K. Carver, and W. C. Schumb, *THIS JOURNAL*, 41, 2019 (1919). Reference will be found in this paper to earlier work of Just, Garelli and Falciola, etc.

The piezometer was suspended in the thermostat for several minutes, and the meniscus set at a height estimated to break contact at a pressure slightly below 100 megabars. The space above the meniscus was filled with water, the platinum point screwed on, cotton placed in the openings at the top, and the piezometer carefully lowered into the pressure cylinder, which was then packed in ice. The further operations were precisely like those which have been so often described before.

Apparently, the density of solid benzene (which is needed for calculating the results) has never been determined. Various values at  $0^\circ$  are given in tables, but if these were directly determined, the measurements must have been made on the under-cooled liquid. On account of the great tendency of the liquid to dissolve air, the measurement of the specific gravity of solid benzene is not very easy. A rough determination made in the 17.82-cc. tube showed that its density is slightly over 1.000. This is confirmed by the very careful determination of the change in volume upon melting of benzene (thoroughly free from air) of Julius Meyer,<sup>5</sup> who found that one gram of benzene increases 0.1333 cc. in volume on melting. If the density of liquid benzene at its melting point is 0.8941, the density of the solid would then be 1.0151. This value (which probably differs only very slightly from the density at  $0^\circ$ ) was used in the following calculation.

Both the benzene and toluene had been very carefully purified. The benzene had been prepared by Dr. J. W. Shipley,<sup>6</sup> and the toluene by Dr. F. Barry.<sup>7</sup>

The compressibility determinations follow. The first three columns give three successive pressure measurements,  $p_0$ ,  $p_1$ ,  $p_2$ ; the next two, the weights of mercury added ( $w$  and  $w_2$ ) to obtain  $p_1$  and  $p_2$ ; the last two columns record the values for the weights calculated for two successive pressure ranges of exactly 200.00 megabars, and the calculation was made

## DATA.

COMPRESSIBILITY OF LIQUID BENZENE AT  $20^\circ$  (E. P. B.)

Density of Benzene ( $20^\circ/4^\circ$ ) = 0.8788; Weight taken 25.016 g.

(Pressures in megabars).

Pressures.			Actual weights mercury.		Calculated weights mercury	
$p_0$	$p_1$	$p_2$	$w_1$	$w_2$	( $w_1$ ) cor. 100-300.	( $w_2$ ) cor. 300-500.
109.5	300.9	...	5.7395	...	6.0269	...
100.4	300.6	500.5	6.0265	5.1592	6.0243	5.1656
100.5	301.0	500.9	6.0298	5.1565	6.0197	5.1652
Average weights of added mercury with benzene in apparatus =					6.0236	5.1654
Average weights with mercury alone filling completely the						
apparatus =					0.3363	0.3313

<sup>5</sup> Julius Meyer, *Z. physik. Chem.*, 72, 225 (1910).

<sup>6</sup> Richards and Shipley, *THIS JOURNAL*, 36, 1830 (1914); also 41, 2022 (1919).

<sup>7</sup> Richards and Barry, *ibid.*, 37, 996 (1915).

COMPRESSIBILITY OF SOLID BENZENE AT 0° (J. H. H.).  
Density of Benzene (0°/4°) = 1.0151, Weight taken 15.685 g.

Pressures.			Actual weights mercury.		Calculated weights mercury.	
$p_1$	$p_2$	$p_3$	$w_1$	$w_2$	( $w_1$ ) cor.	( $w_2$ ) cor.
89.90	292.86	519.06	1.6795	1.7630	1.6511	1.5617
110.37	302.37	488.02	1.5804	1.4364	1.6496	1.5448
108.11	296.63	490.76	1.5619	1.5015	1.6615	1.5399
Average weights of added mercury with benzene in apparatus =					1.6541	1.5488
Average weights of added mercury with glass tube filled with mercury =					0.4836	0.4772

by determining exactly the  $dv/dp$  values at about 100, 300, and 500 megabars in each case, in special trials, but could have been taken from a carefully plotted curve.

Calculated by the equations given in a previous paper<sup>8</sup> these data give the following values for the compressibility of benzene.

#### RESULTS. COMPRESSIBILITY OF LIQUID AND SOLID BENZENE.

	Range 100-300.	Compressibility $\times 10^4$ . Range 300-500.	Range 100-500.
Liquid Benzene at 20.00°.....	77.68	66.46	72.07
Solid Benzene at 0°.....	31.69	29.30	30.49

Evidently the compressibility of the solid is far less than that of the liquid, as is also its decrease with increasing pressure. Of course the comparison should properly be made with each phase at the same temperature; but the compressibility of the liquid cannot be determined at 0°. Some clue as to the effect of changing temperature may be found from the parallel behavior of liquid toluene. In the same apparatus as that used for solid benzene, one of us (E. P. B.) found that with 15.459 g. of toluene  $d_4^{20}$  0.8845) the averaged values of ( $w_1$ ) cor. and ( $w_2$ ) cor. were respectively 3.4397 g. and 3.0370 g. These figures lead to the following values of the compressibility of toluene, which are compared with those previously found <sup>1,9</sup> at 20°.

#### RESULTS. COMPRESSIBILITY OF TOLUENE AT 0° AND 20°.

	Range 100-300.	Compressibility $\times 10^4$ . 300-500.	100-500.
Toluene at 0°.....	65.98	57.61	61.78
Toluene at 20.00°.....	74.07	63.93	69.00

The change of 20° affects the compressibility by about 10 or 11%. Probably the compressibility of benzene would show a somewhat larger

<sup>8</sup> Richards, Stull, Mathews and Speyers, THIS JOURNAL, 34, 980 (1912), on last half of the page.

<sup>9</sup> This value agrees exactly with that found in an earlier research, (*ibid.*, 34, 988, (1912)).

temperature effect, so that its liquid compressibility at  $0^\circ$  would be not far from 0.000063, (over the range 100 to 500 megabars) whereas that of the solid is only 0.0000305 — less than half the former.

The comparison of these results with those of other experimenters is interesting. In the first place, the result 72.07 for benzene at  $20^\circ$  confirms satisfactorily the most recent previous result 72.09 obtained with a quite different form of glass apparatus.<sup>1,10</sup> This indicates consistency, and inspires confidence in both techniques. Evidently the needful precautions against complication by the hysteresis of glass had been properly observed.

Apparently the only earlier determination of the compressibility of solid benzene was that of Harry Essex.<sup>11</sup> He gives as the relative volumes of the substance at  $0^\circ$ , 0.87045, 0.84561 and 0.83277 at 1, 500 and 1000 kg/cm<sup>2</sup>, respectively. The existence of these unusual results, which give an average compressibility  $59. \times 10^{-6}$  over the first range, and  $29.4 \times 10^{-6}$  over the second range, had been among the reasons for the present study. In the light of our data, it seems possible that the benzene used by Essex had not been freed from air, of which he makes no mention. The presence of only about 1.5% by volume of air would account for the wide variation shown by his own figures, as well as the discrepancy between his and ours. In that case his values for the higher pressures are doubtless much more nearly correct than those for the lower pressures.

We are indebted to the Carnegie Institution of Washington for some of the apparatus used in this research.

### Summary.

This brief paper records for the first time an accurate determination of the compressibility of solid benzene at  $0^\circ$ , namely  $(\Delta V/\Delta PV_0)_T = 0.0000305$  over the range 100 to 500 megabars.

Incidentally, the compressibility of liquid toluene at  $0^\circ$  over the same range was found to be 0.0000618.

A new determination of the compressibility of liquid benzene at  $20^\circ$  confirmed satisfactorily the previous determination, giving the value 0.00007207 for the same range.

The compressibility of solid benzene is shown to be less than half that of liquid benzene at the same temperature. Thus another case, supporting the majority of those investigated, is found in which the solid shows much smaller compressibility than the liquid.<sup>12</sup> Interpretation of the result will be postponed until more cases of this kind have been studied.

CAMBRIDGE 38, MASS.

<sup>10</sup> Richards and Shipley, *THIS JOURNAL*, **38**, 998 (1916). An earlier, less carefully found value, 72.4 (*ibid.*, **34**, 340 (1912)), is somewhat higher.

<sup>11</sup> Essex, *Z. anorg. Chem.*, **88**, 200 (1914).

<sup>12</sup> T. W. Richards, *THIS JOURNAL*, **37**, 1648 (1915).



[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

## THE EXISTENCE OF TETRAHYDRATED SODIUM SULFATE IN MIX-CRYSTALS WITH SODIUM CHROMATE.

By THEODORE W. RICHARDS AND W. BUELL MELDRUM.

Received March 11, 1921.

Dekahydrated sodium chromate and sodium sulfate form mix-crystals in almost all, if not all, proportions. The present note proves that the tetrahydrate of sodium chromate also is capable of isomorphously dissolving sodium sulfate, in spite of the fact that  $\text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  does not exist by itself.

The induced crystallization of one salt by a second, in the otherwise unattainable form of hydration of the second, is well known in several other instances: for example, the crystallization of cupric sulfate heptahydrate,  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ , with ferrous sulfate heptahydrate.<sup>1</sup> Nevertheless, cases of this kind are not so numerous as to make the addition of another to their number superfluous: hence the publication of the present brief paper, which records a side-issue of a comprehensive investigation of the sulfate-chromate equilibrium.

That mix-crystallization occurs with sodium chromate tetrahydrate might be inferred from the fact that sodium sulfate is eliminated only very slowly during recrystallization of the tetrahydrate of sodium chromate.<sup>2</sup>

This conclusion was strongly supported by preliminary analysis of crystals of tetrahydrated sodium chromate obtained from warm solutions of sodium chromate containing considerable sodium sulfate, which had been washed four times with a pure saturated solution of sodium chromate while the crystals were stirred with the washing liquid. After crushing and air-drying to the first visible trace of efflorescence, 0.8712 g. of these crystals lost 0.2695 g. (or 30.93%) of water on complete dehydration: and 7.06% of sodium sulfate was found in the residue. The theoretical water content for this mixture if both salts were present in the form of tetrahydrate would be 30.96%, or almost exactly that found.

Evidence that the sulfate thus found was not due to remaining mother liquor was afforded by the fact that the second and fourth wash-solutions contained approximately identical percentages of sulfate. It was necessary to make sure, however, that separate crystals of partly dried ordinary Glauber's salts were not present. Therefore in subsequent trials not only the crystallization but also the filtering, washing with pure saturated

<sup>1</sup> Marignac, *Ann. Mines*, 9, 1 (1856); also Lecoq de Boisbaudran, *Ann. chim. phys.*, 18, 246 (1860). See also Stortenbeker, *Z. physik. Chem.*, 16, 250 (1895); and Retgers, *ibid.*, 16, 580 (1895), and 15, 571 (1894).

<sup>2</sup> T. W. Richards and G. L. Kelley, *Proc. Am. Acad.*, 47, 173 (1911).

chromate solution and drying were conducted about 32.4°. The final drying of the crystals was accomplished by allowing them to stand over dil. sulfuric acid of such concentration that its vapor pressure was slightly less than that of the solution of sodium chromate saturated at the same temperature. Six separate crops of crystals were prepared from different solutions and treated in this way before analysis. Sample 2 consisted of short, fine powdery crystals; Samples 3 and 4, of fine needles; Samples 5 and 6, after drying to constant weight, were afterwards crushed and again placed in the desiccator. Sample 7 was exposed to an atmosphere dry enough to dehydrate crystals containing 10 molecules of water. Samples 8 and 9 consisted of very large, clear crystals crystallized at 23° and picked out carefully by hand.

TABLE I.  
Analysis of Tetrahydrated Mix-crystals.

Sample.	Weight crystallized salt. G.	Weight water. G.	Na <sub>2</sub> SO <sub>4</sub> in anhydrous residue. %.	Per cent. of water. Observed. %.	Calc. for 4H <sub>2</sub> O for both salts. %.
2	1.2785	0.3985	5.08	31.2	30.9
3	2.3503	0.7335	3.25	31.2	30.9
4	2.0832	0.6635	2.97	31.8	30.8
5	0.8716	0.2703	3.25	31.0	30.9
6	1.5546	0.4821	2.97	31.0	30.8
7	1.4003	0.4323	3.07	30.9	30.9
8	1.5940	0.5010	8.58	31.4	31.0
9	1.7098	0.5296	4.39	31.0	30.9

In every case except No. 4 (in which the fine needles had apparently not been adequately dried), the amount of water was within the usual limit of error in such cases. If all the sulfate in Expt. 8 had been dekahydrated, the percentage of water found would have been 35.9, instead of 31.4. There can thus be no question that sodium sulfate crystallizes with sodium chromate in the form of tetrahydrate, Na<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O. The effect of the dissolved sulfate on the crystal angles would be a matter of interest, but time was lacking for its study.

The distribution of sodium sulfate between the crystals and their mother liquor was approximately determined by analysis of mother liquors from new tetrahydrate crystals as follows.

Na <sub>2</sub> SO <sub>4</sub> in dried crystals. %.	Na <sub>2</sub> SO <sub>4</sub> in dried salt from liquid. %.	Temperature of formation. °C.
4.39	10.38	23
2.97	8.00	33

These make no pretension to great accuracy, but show roughly that the sulfate under these conditions is distributed between the crystals and the salts in solution in the ratio 1:2.5, approximately. This is, of course,

a far smaller proportion of sulfate in the crystals than in the case of decahydrate, but is quite enough to account for the difficulty in eliminating sodium sulfate from chromate by crystallization as tetrahydrate.

When sodium sulfate was in large excess, in repeated trials, no crystallization could be induced by inoculating the saturated mixture with the crystal of the tetrahydrate above the transition temperature of sodium sulfate, and below this temperature only crystals of the decahydrate could be made to form. Thus under these conditions the tetrahydrate is so much more soluble than the phases containing more sodium sulfate as to be incapable even of meta-stable existence.

### Summary.

In brief, this paper shows that crystals of  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  dissolve sodium sulfate as  $\text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (a form otherwise unknown) to the extent of somewhat less than half the quantity corresponding to the same weight of sodium chromate in the supernatant solution.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 365.]

## THE SOLUBILITIES OF ACIDS IN AQUEOUS SOLUTIONS OF OTHER ACIDS.

By JAMES KENDALL AND JAMES C. ANDREWS.

Received March 24, 1921.

The factors controlling addition-compound formation in systems of the type  $\text{HX}:\text{HY}$  have been investigated in an earlier article.<sup>1</sup> It has been established that a weak acid in the presence of a strong acid behaves as a base, the stability of the resultant "salt" depending upon the difference in acidic strengths. Precisely the same factors are operative in determining the hydration of an acid in aqueous solution, the extent of compound formation between acid and water increasing uniformly with the strength of the acid.<sup>2</sup> When we come to consider the three-component system  $\text{HX}:\text{HY}:\text{H}_2\text{O}$ , the equilibria involved are naturally more complicated. By investigation of the solubility curve for one acid  $\text{HX}$  in solutions containing increasing concentrations of the second acid  $\text{HY}$ , however, we can obtain valuable evidence with regard to the existence and stability of compounds between the two acids in aqueous solution. The problem resembles in certain respects one already taken up in a previous paper<sup>3</sup>—the effect of other chlorides upon the solubility of silver chloride in water—but is obviously considerably more intricate in view of the wide variations possible in the solubilities and in the ionization constants of the two acids selected.

<sup>1</sup> Kendall, *THIS JOURNAL*, 36, 1722 (1914).

<sup>2</sup> Kendall, Booge and Andrews, *ibid.*, 39, 2303 (1917).

<sup>3</sup> Kendall, Davidson and Adler, *ibid.*, 43, 1496 (1921).

It must be admitted that final conclusions upon systems of this nature cannot be arrived at until considerable advances in our general theory of solutions have been made (at present, the nature of the equilibria in the simple system  $HX:H_2O$  is still debatable), but by the comparison and correlation of typical cases we may hope to gain some insight into the factors concerned which will prove of assistance in the subsequent development of this general theory.

The case where  $HX$  is a typical weak acid and  $HY$  a typical strong acid may be briefly analyzed as an illustration. If no compound formation occurs in aqueous solution, the addition of  $HY$  to a saturated solution of  $HX$  in water theoretically necessitates a sharp dip in the solubility curve of  $HX$  until the "constant undissociated value" is reached,<sup>4</sup> since the ionization of the weak acid will be reduced practically to zero in the presence of the strong acid. Further addition of  $HY$  will have little effect.<sup>5</sup> If compound formation does occur, however, an opposing factor upon the solubility curve is immediately introduced. Addition of  $HY$  now involves the removal of  $HX$  molecules as such from the solution to form molecules of the complex, consequently more solid  $HX$  must dissolve to re-establish equilibrium. The more stable the compound, the more marked will be this effect. In an extreme case it may even wipe out the sharp initial "ionic" decrease in solubility, increasing values being recorded from the very start. If the dissociation of the compound into its components in the solution is extensive,<sup>6</sup> on the other hand, the increase in the solubility may not appear until very high concentrations of  $HY$  are reached. In such a system the solubility curve will exhibit a characteristic minimum.

Other types of solubility curve will result when two acids of similar character are chosen, or when the order of acidic strengths is reversed. Assuming that the generalizations derived from the study of two-component systems are still valid, we may predict the following behavior for the various possible combinations.

(A) $HX$ weak; $HY$ strong	Extensive compound formation	Curve with a minimum
(B) $HX$ weak; $HY$ weak	Little compound formation	Curve variable; generally rising
(C) $HX$ strong; $HY$ strong	Extensive hydration; little compound formation	Curve steadily falling
(D) $HX$ strong; $HY$ weak	Extensive compound formation	Curve generally rising

<sup>4</sup> Nernst, *Z. physik. Chem.*, 4, 372 (1889); Kendall, *Proc. Roy. Soc.*, 85A, 200 (1911). See however Stieglitz, *THIS JOURNAL*, 30, 946 (1908).

<sup>5</sup> The actual course of the curve will depend primarily upon the method employed for expressing concentrations, a point which is discussed in the text later. In general, removal of water as solvent by hydration of the strong acid  $HY$  will result in a gradual further decrease in the solubility of  $HX$ .

<sup>6</sup> In view of the large excess of water present, this may in practically all systems be presumed to be the case.

In systems of the Type B the predominant factor in determining the final course of the solubility curve will be changes in internal pressure, the effect of which has been discussed in detail by Hildebrand and his collaborators in a recent series of articles.<sup>7</sup> If the difference in the internal pressures of HX and HY in the liquid state is smaller than the difference in the internal pressures of HX and H<sub>2</sub>O we may expect the solubility to increase, if it is larger we may predict a decrease. Since most weak acids are organic and closely similar in character, a rising solubility value will be more frequently encountered.<sup>8</sup>

In systems of Type C, where both acids are highly polar, the chief factors will be repression of ionization and removal of solvent water by hydration of the added acid; hence in general a steadily decreasing solubility of the original acid will result. Changes in the degree of hydration as the water concentration diminishes may, however, involve changes in the nature of the stable phase and consequently induce sharp breaks in the curve.

In systems of Type D, finally, the formation of addition compounds will (as in Type A) bring about a continuous increase in solubility after the initial "ionic" effect in the opposite direction is overcome. This initial effect, however, will here be much smaller (often indeed scarcely noticeable), since the weak acid HX will not be appreciably ionized in the presence of excess of the strong acid HY. A generally rising curve may therefore be expected.

The nature of the accordance of the available experimental data with these several predictions will be taken up in a later section, after the results obtained for the systems investigated in this research have been described.<sup>9</sup>

### Experimental.

The solubility curves here examined are : (1) hydrogen sulfide in hydrochloric acid solution; (2) boric acid in hydrochloric acid and nitric acid solutions; (3) benzoic acid in hydrochloric acid and nitric acid solutions; (4) salicylic acid in hydrochloric acid and nitric acid solutions. A series of weak acids with extremely divergent properties was intentionally

<sup>7</sup> See in particular, Hildebrand, *THIS JOURNAL*, 38, 1452 (1916).

<sup>8</sup> Compare Kendall, *Proc. Roy. Soc.*, 85A, 218 (1911).

<sup>9</sup> The experimental part of this paper was completed in 1917. Owing to the absence of one of the authors on naval duty and to the pressure of other work, however, its publication has been delayed. In the interim an important investigation by Knox and Richards (*J. Chem. Soc.*, 115, 508 (1919)) has appeared, in which solubility curves for no fewer than 48 different systems of the various types discussed above are examined. The conclusions of Knox and Richards are in substantial agreement with those here expressed, and their results have been drawn upon freely in illustrating the argument in the later sections of this article.

selected, in the expectation that the comparison of the results obtained would show (a) whether weak acids of widely different acidic strengths<sup>10</sup> give curves of the same type with the same strong acids, (b) whether inorganic and organic acids behave similarly, and (c) whether a gas gives the same type of curve as a solid. In order to obtain additional information with regard to the equilibria existent in mixed acid solutions, conductivity determinations were also carried out on certain of the above systems.

After considerable hesitation as to the best method of expressing concentrations, it was decided to employ volume units (gram molecules solute per liter solution) throughout. The comparison of the results here obtained with those of previous investigators is thereby greatly facilitated.<sup>11</sup> It is recognized that the representation of all compositions in terms of mol fractions is theoretically preferable,<sup>12</sup> but until we know more about the nature of the molecular types present in the solutions here examined the evaluation of their respective mol fractions is not feasible. A possible alternative procedure is to use weight concentrations, *i. e.*, to compare solubilities in a fixed weight of water. This has the disadvantage of neglecting the added acid entirely, and since this frequently exerts a greater solubility effect than water itself, values obtained on this basis for high concentrations of added acid would often be absurdly large. The use of the volume units here adopted, it must be noted, is more apt to lead to errors in the opposite direction, owing to the fact that the molecular volumes of the added acids are, in general, considerably higher than that of water.<sup>13</sup> This is a factor which must be borne in mind throughout in making comparisons, although its exact magnitude for any particular case cannot at present be calculated. It will be partially counterbalanced in all cases by the progressive disassociation of water as the concentration of added acid is increased.

<sup>10</sup> The respective ionization constants in water are:  $\text{H}_2\text{S}$ ,  $k_{18}^\circ = 5.7 \times 10^{-8}$ ;  $\text{H}_3\text{BO}_3$ ,  $k_{25}^\circ = 6.6 \times 10^{-10}$ ;  $\text{C}_6\text{H}_5\text{COOH}$ ,  $k_{25}^\circ = 6.6 \times 10^{-5}$ ;  $\text{C}_6\text{H}_4\text{OH.COOH}$ ,  $k_{25}^\circ = 1.06 \times 10^{-8}$  (Landolt-Börnstein, "Tabellen," 1912, p. 1182, *et seq.*). Boric acid was specifically chosen because of the availability of previous conductivity data for comparison with the results here obtained (see the discussion in a later section); benzoic and salicylic acids, similarly, because of previous solubility determinations.

<sup>11</sup> Density data will be added in a subsequent article, in which the evidence afforded by solution volume changes upon hydration and compound formation will be discussed (compare Bousfield, *J. Chem. Soc.*, 107, 1405 (1915)).

<sup>12</sup> See Kendall, Davidson and Adler, *THIS JOURNAL*, 43, 1481 (1921).

<sup>13</sup> If both water and HY were quite indifferent substances with respect to HX the *mol fraction* of HX in the saturated solution would remain constant as HY replaced  $\text{H}_2\text{O}$ . Hence, if the *average molecular volume* of the solvent increases as HY is added, the *volume concentration* of HX will diminish. Hydration of HY, which will increase the *average molecular volume* of the solvent still further, involves a more rapid diminution, in the volume concentration of HX.

The System  $\text{H}_2\text{S} : \text{HCl} : \text{H}_2\text{O}$ .

A steady current of hydrogen sulfide was obtained by running ammonium sulfide solution into conc. hydrochloric acid.<sup>14</sup> The gas first passed through wash-bottles containing dil. sulfuric acid (to remove ammonia)<sup>15</sup> and concentrated sodium sulfide solution (to remove hydrochloric acid and possible traces of carbon dioxide).<sup>16</sup> It was then bubbled over a long column of aqueous hydrogen chloride solution, of the same concentration and at the same temperature as that in which its solubility was being determined,<sup>17</sup> and thence it was finally passed, by means of a capillary tube, through a standardized solution of hydrochloric acid in an absorption buret, immersed in a Freas thermostat at  $25 \pm 0.01^\circ$ . The lower portion of this buret consisted of a 50-cc. bulb above and below which the tube was calibrated. When equilibrium was established,<sup>18</sup> the buret was disconnected, a known volume of the solution was run out into a measured excess of standardized iodine solution, and the remaining free iodine titrated back by means of sodium thiosulfate.

The results given below express, first of all, the usual absorption coefficient (*i. e.*, the number of volumes of hydrogen sulfide, reduced to  $0^\circ$  and 760 mm., taken up by one volume of the solution under a pressure of hydrogen sulfide<sup>19</sup> of 760 mm.) and secondly the concentration of the saturated solution under the same conditions in gram molecules of hydrogen sulfide per liter. The values shown represent the mean of several determinations at each concentration of hydrochloric acid,<sup>20</sup> checking within 0.2 to 0.3%.

TABLE I.—SOLUBILITY OF  $\text{H}_2\text{S}$  IN AQUEOUS SOLUTIONS OF  $\text{HCl}$ .  $25^\circ$ .

Normality of $\text{HCl}$ solution.	Absorption coefficient.	G. mols of $\text{H}_2\text{S}$ per liter.
0.0	2.266 <sup>a</sup>	0.1023
0.1348	2.253	0.1018
0.2828	2.247	0.1015
0.6308	2.250	0.1016
1.180	2.260	0.1020
1.848	2.272	0.1026
2.498	2.281	0.1030
3.040	2.291	0.1034
3.308	2.301	0.1039
4.410	2.384	0.1076
4.874	2.413	0.1090

<sup>a</sup>Accurate determinations of the solubility of  $\text{H}_2\text{S}$  in water at various temperatures have been made by Winkler, *Z. physik. Chem.*, 55, 350 (1906). Winkler's interpolated value for  $25^\circ$  is 2.257.

<sup>14</sup>It was first attempted to prepare  $\text{H}_2\text{S}$  by treating granulated  $\text{ZnS}$  with  $\text{HCl}$  in a Kipp generator. The  $\text{ZnS}$  available, however, varied too much in quality to give consistent results.

<sup>15</sup>Subsequent tests showed this to be unnecessary.

<sup>16</sup>Four wash-bottles were used; at the end of the experiments all except the first gave negative tests for chloride and carbonate.

<sup>17</sup>This was done in order to bring the gas to equilibrium with the final solution in advance, so avoiding concentration changes in this solution during determinations.

<sup>18</sup>With the apparatus employed it was found that absorption was complete in 2 or 3 hours.

<sup>19</sup>Pressure corrections were necessary for the vapor tension of the solution, the barometric pressure at the time of the experiment, and the average head of liquid over the portion of the solution titrated. The weight of 1 liter of  $\text{H}_2\text{S}$  under standard conditions was taken as 1.5392 g. (Baume and Perrot, *J. chim. phys.*, 6, 610 (1909).)

<sup>20</sup>The change in volume of the solution (and hence the change in  $\text{HCl}$  concentration) during absorption of the  $\text{H}_2\text{S}$  was found to be negligible.

The solubility curve evidently shows a minimum at about 0.4 *N* hydrochloric acid, and for concentrations of hydrochloric acid above 1.5 *N* the solubility of hydrogen sulfide is (contrary to the prevalent opinion) greater than in pure water. A still more rapid increase in solubility was found by Pollitzer<sup>21</sup> for hydrogen sulfide in aqueous solutions of hydrogen iodide; unfortunately the lack of data for concentrations of hydrogen iodide below 1 *N* obscures the position of the probable minimum.

Solubility determinations for hydrogen sulfide in other common strong acids (nitric and sulfuric) cannot be made, owing to their rapid oxidizing action. Even the presence of dissolved oxygen in the hydrochloric acid solutions here employed resulted in the slow precipitation of minute amounts of free sulfur from the solutions. This was minimized by boiling the solutions vigorously before standardization and exposing them to the air as little as possible before use.

The results of conductivity measurements<sup>22</sup> upon this system were entirely negative. Over a series of concentrations of hydrochloric acid ranging from 0.0074 *N* to 4.410 *N*, saturation of the solution with hydrogen sulfide produced no measureable change in the bridge reading.

### The System $\text{H}_3\text{BO}_3 : \text{HCl} : \text{H}_2\text{O}$ .

Standardized hydrochloric acid solutions were rotated with excess of powdered boric acid (purified by recrystallization from water) in the thermostat until saturation was reached. Samples of the clear solutions were pipetted out into tared porcelain crucibles and dried to constant weight at 60°. The boric acid content of the final solutions was thus directly obtained; the small changes in hydrochloric acid concentration involved in the increase of volume during solution of boric acid were corrected for by interpolated density determinations. Attempts to make a differential titration of the two acids in the final solution, as recommended by Herz,<sup>24</sup> were not satisfactory.

The results of conductivity determinations upon the saturated solutions, and upon hydrochloric acid solutions of the same concentrations, are included in the table below. Specific conductivities are expressed in reciprocal ohms throughout.

As will be seen from the figures in the second column,<sup>25</sup> a solubility minimum is again obtained, but only at a very high concentration (about 8.0 *N* hydrochloric acid). The conductivity changes due to the presence of dissolved boric acid are quite con-

<sup>21</sup> Pollitzer, *Z. anorg. Chem.*, 64, 121 (1909).

<sup>22</sup> A 3-meter Leeds and Northrup bridge was employed. Alternating current at 1000 cycles per second was obtained from a constant-speed high-frequency generator. The telephone receiver was tuned to the same frequency. The conductivity cell was of the Cantor type (Cantor, *Z. Elektrochem.*, 9, 922 (1903)).

<sup>23</sup> Preliminary trials with boric acid solutions of known concentration established the fact that this temperature was low enough to preclude appreciable loss of  $\text{H}_3\text{BO}_3$  by volatilization during evaporation.

<sup>24</sup> Herz, *Z. anorg. Chem.*, 33, 353 (1903).

<sup>25</sup> These values are not in accordance with those obtained by Herz (*loc. cit.*, p. 355) for the same system, although the form of the curve is precisely similar. The fact that Herz made no correction for changes in concentration of the solvent acid during solution of  $\text{H}_3\text{BO}_3$  is presumably the cause of this disagreement. Herz obtained the concentration of  $\text{H}_3\text{BO}_3$  in each solution from the difference between original and final titrations, and with very high concentrations of HCl a small total error involves a considerable error in  $\text{H}_3\text{BO}_3$ .



TABLE II.— $\text{H}_3\text{BO}_3$  IN AQUEOUS  $\text{HCl}$ . SOLUBILITY AND CONDUCTIVITY DATA.  $25^\circ$ .

Normality of $\text{HCl}$ soln.	$\text{H}_3\text{BO}_3$ dissolved (g. mols per liter).	Spec. cond. of $\text{HCl}$ soln.	Spec. cond. of final solution.	Decrease due to $\text{H}_3\text{BO}_3$ .
0.0	0.8950 <sup>a</sup>	.....	.....	.....
0.0660	0.8810	0.02599	0.02368	0.0023
0.1302	0.8580	0.04953	0.04494	0.0046
0.2733	0.8380	0.09740	0.08833	0.0091
0.6112	0.7761	0.1943	0.1774	0.0169
1.147	0.7042	0.3104	0.2854	0.0250
1.802	0.6270	0.4068	0.3768	0.0300
2.617	0.5431	0.4880	0.4603	0.0277
3.126	0.4976	0.5271	0.5013	0.0268
4.336	0.4189	0.5788	0.5539	0.0249
5.160	0.3715	0.5804	0.5606	0.0198
7.073	0.3446	.....	.....	.....
9.389	0.3501	.....	.....	.....
11.56	0.3687	.....	.....	.....

<sup>a</sup>The values obtained by previous investigators are extremely discordant (see Seidell, "*Solubilities of Inorganic and Organic Compounds*," 1919, p. 153). The result here obtained, however, agrees fairly well with the more recent data (*e. g.*, 0.901 *N* (Herz) and 0.887 *N* (Ageno and Valla)).

siderable, as evidenced by the results in the last column. The decreases recorded cannot be entirely ascribed to viscosity changes in the solution, although direct experiment showed that the viscosities of boric acid solutions near the saturation point<sup>26</sup> are considerably higher than that of pure water, since the corresponding benzoic acid systems (see below) where the viscosity effect is negligible, exhibit exactly the same behavior. Their significance will be taken up in a later section.

### The System $\text{H}_3\text{BO}_3 : \text{HNO}_3 : \text{H}_2\text{O}$ .

The experimental procedure was exactly as in the previous system; solubility and conductivity results obtained are given in Table III below.

TABLE III.— $\text{H}_3\text{BO}_3$  IN AQUEOUS  $\text{HNO}_3$ . SOLUBILITY AND CONDUCTIVITY DATA.  $25^\circ$ .

Normality of $\text{HNO}_3$ soln.	$\text{H}_3\text{BO}_3$ dissolved (g. mols per liter).	Spec. cond. of $\text{HNO}_3$ soln.	Spec. cond. of final soln.	Decrease due to $\text{H}_3\text{BO}_3$ .
0.0	0.8950	.....	.....	.....
0.0779	0.8820	0.02951	0.02673	0.0028
0.1951	0.8610	0.07100	0.06409	0.0069
0.5337	0.8028	0.1726	0.1553	0.0168
0.9890	0.7361	0.2783	0.2528	0.0255
1.580	0.6685	0.3766	0.3469	0.0297
2.372	0.5943	0.4774	0.4429	0.0345
3.118	0.5444	0.5319	0.5021	0.0298
3.806	0.4977	0.5634	0.5350	0.0284
4.698	0.4471	0.5811	0.5572	0.0239
8.41	0.2963	.....	.....	.....
10.95	0.2305	.....	.....	.....
15.81	0.1973	.....	.....	.....

<sup>26</sup>Experiments with a Bingham viscometer at  $25^\circ$  (carried out by Dr. J. J. Beaver) gave the following results:  $\text{H}_3\text{BO}_3$  0.6448 molar,  $d_4^{25}$  1.0096, relative viscosity 1.0603;  $\text{H}_3\text{BO}_3$  0.8 molar,  $d_4^{25}$  1.0160, relative viscosity 1.0833.

When the solubility results of the second column are plotted on a diagram, it becomes evident that the minimum on the curve is approximately at the last concentration examined—about 16.0 *N*. The decrease in specific conductivity of the solutions due to dissolved boric acid is similar to that shown in the preceding table.

### The System $C_6H_5.COOH:HCl:H_2O$ .

Solubility determinations were carried out as described in the case of boric acid above, the only difference (necessitated by the greater volatility of the benzoic acid) being that the solutions were allowed to evaporate to constant weight in a desiccator at room temperature. The residues gave no test for chloride.

The solubility and conductivity results obtained are tabulated as before. The correction in the hydrochloric acid concentration for volume change during solution is here inappreciable, owing to the low solubility of benzoic acid.

TABLE IV.—BENZOIC ACID IN AQUEOUS HCl. SOLUBILITY AND CONDUCTIVITY DATA. 25°.

Normality of HCl soln.	Normality of dissolved $C_6H_5.COOH$ .	Spec. cond. of HCl soln.	Spec. cond. of final soln.	Decrease due to $C_6H_5.COOH$ .
0.0	0.0276*	.....	.....	.....
0.2828	0.0254	0.1003	0.0821	0.0182
0.6308	0.0235	0.1992	0.1659	0.0333
1.180	0.0211	0.3162	0.2740	0.0422
1.848	0.0185	0.4119	0.3683	0.0436
3.308	0.0153	0.5234	0.4922	0.0312
4.410	0.0140	0.5808	0.5580	0.0228
5.238	0.0130	.....	.....	.....
7.172	0.0113	.....	.....	.....
9.522	0.0109	.....	.....	.....

\*Philip and Garner (*J. Chem. Soc.*, 95, 1466 (1909)) obtained the value 0.0277.

Once more a solubility minimum at a high concentration of solvent acid (approximately 8.5 *N*) is indicated. The decrease in conductivity due to the presence of the solute acid is, as in the case of the boric acid systems, quite considerable.

### The System $C_6H_5.COOH:HNO_3:H_2O$ .

Measurements for this system were not extended beyond 5.0 *N* nitric acid, since it was desired to avoid nitration effects.<sup>27</sup>

TABLE V.—BENZOIC ACID IN AQUEOUS  $HNO_3$ . SOLUBILITY AND CONDUCTIVITY DATA. 25°.

Normality of $HNO_3$ soln.	Normality of dissolved $C_6H_5.COOH$ .	Spec. cond. of $HNO_3$ soln.	Spec. cond. of final soln.	Decrease due to $C_6H_5.COOH$ .
0.0	0.0276	.....	.....	.....
0.0208	0.0272	0.00838	0.00787	0.0005
0.0807	0.0269	.....	.....	.....
0.1351	0.0268	.....	.....	.....
0.2021	0.0268	0.07338	0.06908	0.0043

<sup>27</sup> Careful tests for nitrogen on the benzoic residues gave negative results in all cases except for the last concentration examined, where nitration was just becoming appreciable.

TABLE V.—(Continued).

Normality of HNO <sub>3</sub> soln.	Normality of dissolved C <sub>6</sub> H <sub>5</sub> .COOH.	Spec. cond. of HNO <sub>3</sub> soln.	Spec. cond. of final soln.	Decrease due to C <sub>6</sub> H <sub>5</sub> .COOH.
0.5514	0.0270	0.1772	0.1652	0.0120
1.019	0.0271	.....	.....	.....
1.623	0.0272	0.3827	0.3656	0.0171
2.430	0.0275	0.4832	0.4658	0.0174
3.883	0.0277	0.5657	0.5573	0.0084
4.784	0.0284	.....	.....	.....

The minimum in the solubility curve is here at a much lower concentration of the solvent acid—about 0.2 *N*. The conductivity results, however, again closely resemble those of the corresponding hydrochloric acid system.

### The System C<sub>6</sub>H<sub>4</sub>OH.COOH : HCl : H<sub>2</sub>O.

This system has already been investigated by Kendall<sup>28</sup> and by Knox and Richards,<sup>29</sup> the results here presented are in fair agreement with their values. The experimental procedure was essentially that followed in the case of benzoic acid systems.

TABLE VI.—SALICYLIC ACID IN AQUEOUS HCl. SOLUBILITY AND CONDUCTIVITY DATA.

Normality of HCl soln.	Normality of dis- solved salicylic acid.	Spec. cond. of HCl soln.	Spec. cond. of final solution.	Decrease due to salicylic acid.
0.0	0.0162 <sup>b</sup>	.....	.....	.....
0.500	0.0112	.....	.....	.....
1.180	0.0101	0.3162	0.3168	0.0006 <sup>a</sup>
1.848	0.00912	0.4119	0.4134	0.0015 <sup>a</sup>
2.498	0.00834	0.4749	0.4805	0.0056 <sup>a</sup>
3.308	0.00777	0.5234	0.5423	0.0189 <sup>a</sup>
4.410	0.00732	0.5808	0.6122	0.0314 <sup>a</sup>
7.172	0.00695	.....	.....	.....
9.522	0.00721	.....	.....	.....
11.73	0.00768	.....	.....	.....

<sup>a</sup> Increase in specific conductivity

<sup>b</sup> The previous values for the solubility in pure water are 0.01634 (Kendall) and 0.01613 (Knox and Richards).

A very flat minimum in the solubility curve is obtained at about 6.0 *N* hydrochloric acid; the conductivity results, however, differ from those of the previous tables in that an increase, instead of a decrease, is induced by the solute acid. This increase is negligible at low concentrations, but becomes very marked above 2.0 *N* hydrochloric acid.

### The System C<sub>6</sub>H<sub>4</sub>OH.COOH : HNO<sub>3</sub> : H<sub>2</sub>O.

The solubility curve for this system could not be carried very far, owing to rapid nitration of the salicylic acid at concentrations of nitric acid above 0.5 *N*.

<sup>28</sup> Kendall, *Proc. Roy. Soc.*, [A] 85, 204 (1911).

<sup>29</sup> Knox and Richards, *loc. cit.*

TABLE VII.—SOLUBILITY OF SALICYLIC ACID IN AQUEOUS SOLUTIONS OF  $\text{HNO}_3$ .

Normality of $\text{HNO}_3$ soln.	Normality of dissolved salicylic acid.	Normality of $\text{HNO}_3$ soln.	Normality of dissolved salicylic acid.
0.0	0.0162	0.2408	0.0141
0.0109	0.0149	0.5514	0.0150
0.0420	0.0140	1.019	0.0184
0.0807	0.0139	.....	.....

The minimum on the curve is here at a very low concentration of solvent acid—less than 0.1 *N* nitric acid. Above 0.5 *N* the results are only approximate, since the residues obtained were appreciably nitrated. For this reason no conductivity determinations were attempted on this system.

### Discussion of Solubility Results.

The solubility curves for a number of systems of the general type  $\text{HX}:\text{HY}:\text{H}_2\text{O}$  are represented in Figs. 1, 2 and 3 below. In the first two diagrams the solvent acid is hydrochloric. The curves for the 4 solute

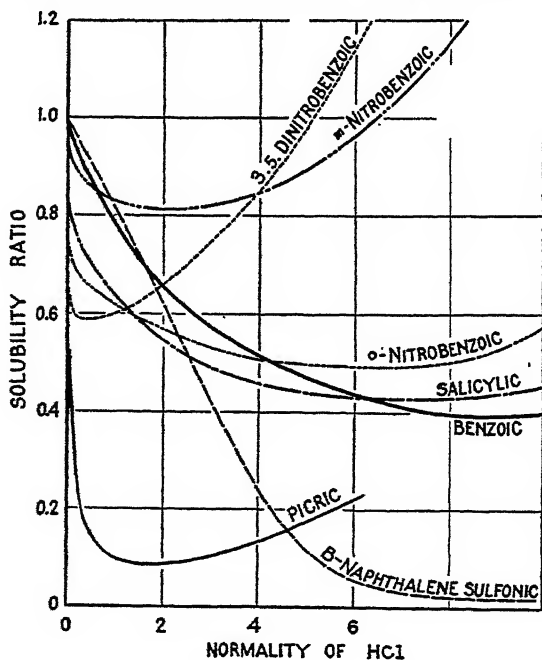


Fig. 1.

acids here investigated are shown, and a selection of the data from previous articles<sup>30</sup> has been added to assist in the discussion. In the third diagram

<sup>30</sup> Most of the data are due to Knox and Richards (*loc. cit.*). Results by Masson (*J. Chem. Soc.*, 101, 103 (1912)); Stepanov (*Ann.*, 373, 221 (1910)); Geffcken (*Z. physik. Chem.*, 49, 254 (1904)), and Herz (*Z. anorg. Chem.*, 34, 205 (1903)) are also included.

the solvent acid is acetic, a weak acid. To render all results directly comparable, the solubilities are expressed throughout as ratios of the solubility at any given concentration to the solubility in pure water.

At first glance it seems hopeless to attempt to draw any significant general conclusions from the course of the curves; they appear to run almost at random. Closer inspection, however, enables us to note the following facts.

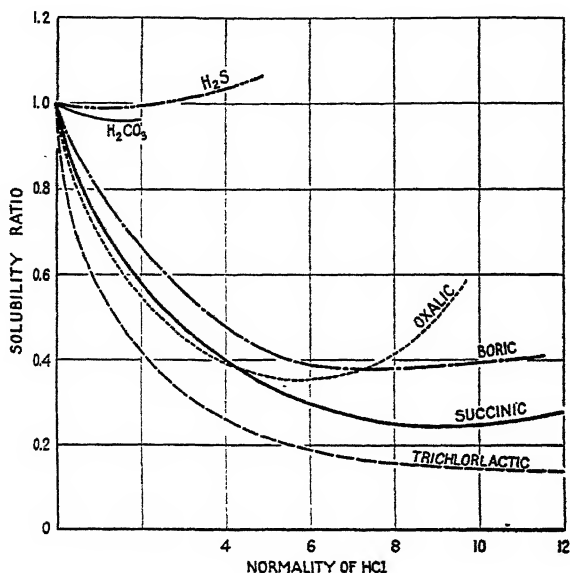


Fig. 2.

(1) When the solvent acid is strong, the sudden initial "ionic dip" in solubility is very marked in all cases except (a) when the solute acid is very weak, or (b) when the solute acid is very soluble in pure water. In Fig. 1 benzoic acid falls under (a),  $\beta$ -naphthalene sulfonic acid under (b). The remaining acids all show a very sharp solubility decrease when hydrochloric acid is first added. That this decrease is due to the suppression of their ionized fractions is evident from the variation in its magnitude as the strength of the solute acid is changed. Thus for picric acid the decline is exceedingly abrupt; it becomes less and less violent as we proceed through the weaker nitrobenzoic acids, until for benzoic acid it is almost absent. With this acid (see also succinic acid in Fig. 2) the solubility falls off regularly as the concentration of hydrochloric acid increases, there is only a trace of a sharp introductory drop. This is only natural, and since there is only a very small ionic portion to repress in such weak acids, inversely, the regularity of the decline in the case of the more soluble stronger acids (e. g.,  $\beta$ -naphthalene sulfonic in Fig. 1, oxalic and trichloro-

lactic in Fig. 2) is to be ascribed to the fact that their ionic concentrations in pure water are too high to be annihilated suddenly by small additions of hydrochloric acid: the suppression of their ionized fractions is consequently a gradual process.

(2) When the solvent acid is weak, the ionic dip is (as might be expected) much less frequently recognizable. In Fig. 3 oxalic acid shows a brief initial solubility decrease; more distinct evidence would, no doubt, be given by less soluble strong acids (*e.g.*, picric) in acetic acid solutions, but confirmatory experimental data are lacking.

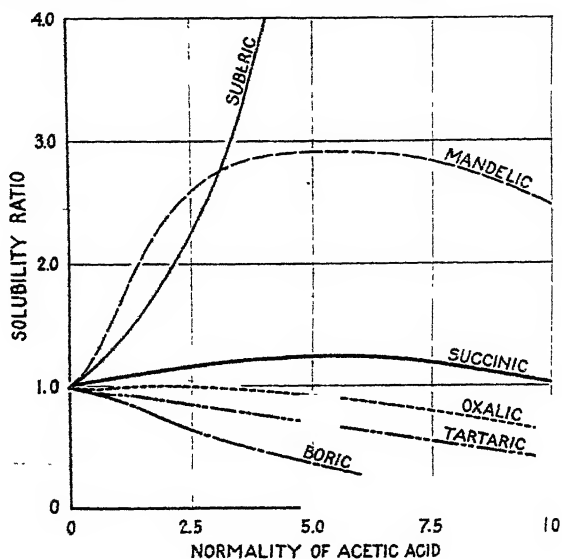


Fig. 3.

(3) When the solvent acid is strong, the decline in solubility persists in all cases well beyond the "constant undissociated value" postulated by Nernst. Thus the solubility ratios for weak acids such as boric acid and benzoic acid fall below 0.4 at high concentrations of hydrochloric acid, although their saturated solutions in pure water are only very slightly ionized. Similarly the solubilities of transition acids (*e.g.*, salicylic, *o*-nitrobenzoic) undergo an abnormal decrease, as indicated in a previous article,<sup>31</sup> while that for  $\beta$ -naphthalene sulfonic acid approaches very closely to zero. This characteristic in the curves must be ascribed to extensive hydration of the solvent acid (hydrochloric acid), as indicated in the introductory sections.<sup>32</sup>

<sup>31</sup> Kendall, *Proc. Roy. Soc.*, [A] 85, 217 (1911).

<sup>32</sup> The solubility of a weak base (ammonia) in water is similarly depressed to an abnormal extent on addition of a strong base (potassium or sodium hydroxide), as has been shown by Abegg and Riesenfeld (*Z. physik. Chem.*, 40, 84 (1902)). In the

(4) When the solvent acid is strong, the excessive decline is in all cases but one followed, at high concentrations, by an increase in solubility. The single exception is  $\beta$ -naphthalene sulfonic acid in hydrochloric acid; this must be regarded as a typical example of a system containing 2 strong acids.<sup>33</sup> The change in direction in all other systems<sup>34</sup> can be explained only on the basis of compound formation between the two acids present. Its late appearance indicates that such compounds are in general, highly dissociated in aqueous solution, but this again is only to be expected, since water is a competing base, stronger and present in much higher concentration. Hydration will therefore outbalance compound formation between the acids until the water concentration is considerably reduced. No connection can be established at present between the position or the sharpness of the minimum and the relative strengths of the two acids. We should anticipate that the weaker the solute acid the greater its tendency to combine with hydrochloric acid, but even such weak acids as hydrogen sulfide<sup>35</sup> and boric acid give a very flat minimum, while stronger acids such as 3,5-dinitrobenzoic and oxalic show a sharp turn in the curve. The very variable solubilities of the different solute acids in pure water certainly introduce complicating factors here for which it is difficult to correct,<sup>36</sup> and more work is evidently necessary to elucidate the irregularities exhibited.

(5) When the solvent acid is weak, the course of the curves is extremely variable (see Fig. 3). Changes in internal pressure and in the average molecular volume of the solvent here seem to be the predominant factors in affecting solubilities, so long as the solute acid is also weak. When the solute acid is strong, we should expect compound formation to be indicated by a rising portion on the solubility curve. Data for this type are, however, not very plentiful. Boric acid, which gives a falling curve in acetic acid solutions, does show steadily increasing solubility values with

same way, the solubility of a non-electrolyte in water is lowered by the presence of a hydrated second solute. Thus Geffcken (*ibid.*, 49, 268 (1904)) found the solubility of hydrogen to fall off rapidly in the presence of strong acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ). Transition acids (chloro-acetic) induce a smaller decrease; weak acids (acetic) have still less effect. Compare also Philip, *Trans. Faraday Soc.*, 3, 140 (1907).

<sup>33</sup> Other systems of a similar character, with the same type of curve, are  $\text{HCl}$  in  $\text{H}_2\text{SO}_4$  solutions (Coppadoro, *Gazz. chim. ital.*, II 39, 625 (1909)), and  $\text{HIO}_3$  in  $\text{HNO}_3$  solutions (Groschuff, *Z. anorg. Chem.*, 47, 344 (1905)).

<sup>34</sup> The curves given by the gaseous solutes are of substantially the same type as those given by solid acids. No marked difference in behavior, moreover, can be noted between inorganic and organic acids.

<sup>35</sup> Baume and Georgitses (*J. chim. phys.*, 12, 242 (1914)) did not isolate any compounds from the system  $\text{HCl}:\text{H}_2\text{S}$ , but found that a continuous series of solid solutions was formed.

<sup>36</sup> Compare Knox and Richerds, *op. cit.*, p. 530.

stronger organic acids such as oxalic,<sup>37</sup> lactic<sup>38</sup> and tartaric,<sup>39</sup> but this may be due in the case of the last two acids to a special effect, as will appear in the following section.

### Discussion of Conductivity Results.

Compound formation between a weak acid and a strong acid in aqueous solution may be predicted to bring about a decrease in specific conductivity at the lower concentrations here examined,<sup>40</sup> since the mobilities of the ions of the resultant *salt*<sup>41</sup> will not equal those of the strong acid which have disappeared in its formation. At the higher concentrations, on the other hand, where the salt is produced mainly at the expense of non-ionized acid, the decrease will tend to diminish.

This anticipated behavior is actually realized in Tables II to V of this paper, *i. e.*, for solutions of boric and benzoic acids in hydrochloric and nitric acids. The specific conductivity changes in all 4 series, due to the presence of the dissolved weak acid, are substantially as described above. At low concentrations the decrease is roughly proportional to the product of the concentrations of the two acids. It reaches a maximum at approximately 2.0 *N* concentration of strong acid and subsequently exhibits declining values.

Not all of those systems, however, which indicate the existence of compound formation by the solubility curves give similar conductivity results. Thus the conductivity of hydrochloric acid solutions is unaffected, within the limits of experimental error, by the presence of hydrogen sulfide. In the same way, it was found that saturation of hydrochloric or nitric acid solutions with other gases of a weakly acidic nature—such as carbon dioxide or acetylene—involved no measurable change in their specific conductivities, although very careful determinations were made and all possible precautions taken to establish small variations.<sup>42</sup> No theoretical reason for this uniformity of negative results with gaseous solutes can at present be suggested.

<sup>37</sup> Herz, *Z. anorg. Chem.*, **66**, 93 (1910). Oxalic acid is also more soluble in boric acid solutions than in pure water.

<sup>38</sup> Mueller and Abegg, *Z. physik. Chem.*, **57**, 514 (1906).

<sup>39</sup> Herz, *Z. anorg. Chem.*, **70**, 71 (1911).

<sup>40</sup> At extremely low concentrations of strong acid, it must be noted, addition of the weak acid involves a small *increase* in specific conductivity, since its ionization will not be significantly repressed. This effect was confirmed for all systems at concentrations of HCl or HNO<sub>3</sub> below 0.005 *N*, but since the present discussion is restricted to much higher concentrations, further consideration of this point is not necessary here.

<sup>41</sup> That addition compounds of this type exhibit electrolytic dissociation in solution has been proved by Rördam, *THIS JOURNAL*, **37**, 557 (1915).

<sup>42</sup> At extremely low concentrations of the strong acid, as explained in the preceding note, a very small increase in specific conductivity is obtained. (Compare Whetham, *Z. physik. Chem.*, **55**, 200 (1906); Drucker, *Z. Elektrochem.*, **13**, 81 (1907)).



In solutions of salicylic acid in hydrochloric acid, an inverse effect— increase in specific conductivity—is actually apparent. If this increase were most noticeable at low concentrations of hydrochloric acid, it might be explained as due to the persistence of ionized salicylic acid in the solutions. At low concentrations, however, the effect is practically absent; it is only at higher concentrations of hydrochloric acid, where the concentration of salicylic acid has decreased far beyond its "constant undissociated value," that the increase in specific conductivity becomes appreciable. It becomes necessary, therefore, to seek an alternative explanation for the anomalous behavior of this system.

Magnanini<sup>43</sup> found that addition of small amounts of polyhydric alcohols increased the specific conductivity of boric acid solutions, owing to the formation of more readily ionized complexes. He also discovered that while addition of boric acid to aqueous solutions of organic acids caused no change in specific conductivity if these acids contained no hydroxyl group, yet a noticeable increase was obtained with aliphatic acids possessing an hydroxyl group in the  $\alpha$ -position and with aromatic acids possessing an hydroxyl group in the *ortho* position. More extensive investigations in this field have recently been made by Böeseken and his co-workers.<sup>44</sup> In view of their results, which indicate that the complexes formed by boric acid and suitable weak organic acids are comparable in strength with the strongest inorganic acids, it would seem logical to ascribe the increase here observed in the system salicylic acid (*o*-hydroxy-benzoic acid)—hydrochloric acid at high concentrations to the formation of an especially highly-ionized complex of a similar character. The examination of additional systems of this type by the conductivity method is obviously necessary, however, before final conclusions can be drawn.

Combination of solubility and conductivity data furnishes us, it may be noted, with a very strong method of attacking the question of the laws governing compound formation in systems of the type weak acid (solute): strong acid (solvent), here particularly studied. From the solubility results we can establish the effect of the strong acid on the weak acid, from the conductivity results the effect of the weak acid on the strong acid. The correlation of the data from sufficient systems should enable us, therefore, to obtain some insight into what is at present a very confused portion of the field of aqueous solutions. In all such investigations, however, the effect of the third component—water—upon all of the equilibria involved must, in addition, be much more intensively examined.

<sup>43</sup> Magnanini, *Gazz. chim. ital.*, 20, 448 (1890); 21, 215 (1891); 22, 541 (1892); 23, 197 (1893).

<sup>44</sup> Böeseken, *et al.*, *Rec. trav. chim.*, 35, 211, 309 (1916) and subsequent papers.

### Summary.

The solubility curves for hydrogen sulfide, boric acid, benzoic acid and salicylic acid in aqueous solutions of hydrogen chloride, and for the last three of the above mentioned weak acids in aqueous solutions of nitric acid, have been determined. The changes in the specific conductivities of the solvent acids, due to the presence of the weak acids in solution, have also been investigated.

The results obtained, together with those of previous investigators, have been critically discussed in connection with the rule, established in an earlier article, that compound formation between acids in pairs increases in extent with increasing diversity of acidic strengths. The predicted and observed solubility curves for systems of various types have been compared, and satisfactory agreement, in general, has been obtained. The conductivity results also fall into line in most cases. Further experimental work, however, is required to elucidate certain abnormalities in particular systems. To establish the rules here outlined upon a final basis, a better understanding of the part played by the third component—water—is also necessary.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

## A MODIFIED METHOD FOR THE DETERMINATION OF IRON AND VANADIUM AFTER REDUCTION BY HYDROGEN SULFIDE.<sup>1</sup>

BY G. E. F. LUNDELL AND H. B. KNOWLES.

Received March 29, 1921.

### I. Introduction.

Some time ago the authors had occasion to determine whether uranyl compounds suffered reduction when their ammoniacal solutions were saturated with hydrogen sulfide and then slightly acidified with sulfuric acid and boiled. Experiments were accordingly carried out which demonstrated that while there was no reduction of uranium, some compound was formed in sufficient amount to consume appreciable quantities of a potassium permanganate solution. It was suspected that this reduction was occasioned by polythionic acids which had been formed during the course of the reactions and it was realized that if such was the case, the observation would be of importance in operations dealing with sulfide reductions in general and those of iron and vanadium in particular.

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

A search of the literature revealed considerable differences in the methods recommended for hydrogen sulfide reductions and in three researches direct evidence was found that the method was subject to error. The conclusions reached in these researches have been practically buried because one research was published under the broad title "The Determination of Iron in Iron Ores" in a foreign journal, another appeared under the title "Contributions to the Volumetric Determination of Antimony, Tin, Titanium, Iron and Uranium" in a privately printed doctorate dissertation, while the third was unpublished.

## II. Historical.

Fresenius-Cohn<sup>2</sup> specify that the cold ferric solution containing a liberal excess of sulfuric acid be reduced by hydrogen sulfide in a flask two-thirds filled until the color disappears and the passage of gas be then continued for at least 10 minutes. The solution is boiled until reduced to  $\frac{1}{2}$  its first volume, and finally diluted with cold water until the flask is nearly filled.

Treadwell-Hall<sup>3</sup> outline two procedures as follows.

(1) The solution of the ferric sulfate containing 10% (by volume) of sulfuric acid is boiled, reduced with hydrogen sulfide until colorless, and the boiling then continued as a current of carbon dioxide is swept through to expel the hydrogen sulfide. (2) The cold sulfuric acid solution (acidity not stated) is saturated with hydrogen sulfide, heated to boiling, and filtered into a flask containing carbon dioxide. The filtrate is boiled as a current of carbon dioxide is passed through and the solution finally cooled in a stream of the gas. In addition it is stated on page 609, "By means of the latter (hydrogen sulfide) the ferric salt is completely reduced, independent of how little or how much free acid is present in the solution."

Gooch<sup>4</sup> directs that the acidified iron solution be boiled, treated to complete reduction with hydrogen sulfide, and the gas expelled by boiling with carbon dioxide.

Scott<sup>5</sup> advocates the use of the filtrate from the hydrogen sulfide group separation, after boiling out hydrogen sulfide.

Mellor<sup>6</sup> merely states that "hydrogen sulfide can be used for reducing the iron," and is obviously not enthusiastic concerning its use.

Washington<sup>7</sup> specifies that the gas be passed through the cold sulfuric acid solution, (acidity not defined), the solution filtered, boiled while carbon dioxide is passed through, and cooled under the same gas.

<sup>2</sup> Fresenius-Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, 1, p. 326 (1904).

<sup>3</sup> Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, 4th Ed., 2, pp. 99, 115.

<sup>4</sup> Gooch, "Representative Procedures in Quantitative Chemical Analysis," John Wiley and Sons, 1st Ed., p. 142.

<sup>5</sup> Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., 2nd Ed., p. 215.

<sup>6</sup> Mellor, "A Treatise on Quantitative Inorganic Analysis," C. Griffin and Co., 1, p. 191 (1913).

<sup>7</sup> Washington, "The Chemical Analysis of Rocks," John Wiley and Sons, 3rd Ed., pp. 163-165.

Hillebrand<sup>8</sup> directs that the cooled solution containing 1.5 to 2.5% by volume of sulfuric acid be treated with hydrogen sulfide, boiled with continued passage of the gas until the sulfur is coagulated, cooled during continued passage of the gas, filtered, treated again with hydrogen sulfide, then boiled and cooled while a current of carbon dioxide is passed through the solution.

R. Fresenius<sup>9</sup> in an article on the determination of iron in iron ores by the Reinhardt method, noted that filtrates from the hydrogen sulfide separation of copper from iron were apt to give high values when subsequently titrated with permanganate. He reached the conclusion that satisfactory results could be obtained by the complete oxidation with permanganate of the hydrogen sulfide filtrate, followed by reduction with stannous chloride and final titration in accordance with the Reinhardt method.

Boller<sup>10</sup> quoted a private communication from Dr. Herrmann to Dr. Treadwell to the effect that values obtained by Hillebrand's method were too high. Work subsequently done by Boller demonstrated that 500 cc. of 1*N* sulfuric acid solution, treated with 1.0 cc. of a saturated sulfur dioxide solution and then as in Hillebrand's method required 2.9 cc. of 0.01 *N* permanganate solution; practically the same values were obtained with sulfur present as with sulfur filtered off. Boller demonstrated by experiments with purified sulfur treated under like conditions that the reducing compounds obtained above were not entirely due to polythionic acids formed by the action of hydrogen sulfide on sulfur dioxide. Further tests of the method carried on with a standard solution of ferric chloride in hydrochloric acid with final titration in the presence of Zimmermann-Reinhardt solution gave results which averaged 0.1040 g. of iron with no filtration of sulfur, 0.1041 g. of iron with filtration of sulfur through paper, and 0.1040 g. of iron with filtration of sulfur through a Gooch crucible, as against a true value of 0.1020 g. of iron.

McBride,<sup>11</sup> in a series of experiments dealing with the reduction of iron by hydrogen sulfide, arrived at the following conclusions.

"It should be noted that the limits of acidity at the time of reduction are given as 2.00 to 2.5%. Any variation from these limits introduces an error. If more than 2.5% volume of free sulfuric acid is present the iron cannot be completely reduced. The use of less than 2.0% by volume of free acid, however, is not permissible, as with the less strongly acidified solution, some compounds having a reducing action on potassium permanganate are formed which are not removable by the boiling with carbon dioxide before titration. The smaller the amounts of free acid, the higher the amount of iron indicated by the titration."

The above citations, particularly the last three, demonstrated the need of an investigation of the hydrogen sulfide reduction and full publicity of the results obtained. This is all the more important since the method is often recommended and widely used on account of such considerations as enumerated by Washington.<sup>7</sup> "This (hydrogen sulfide) commends itself on account of its certainty and rapidity of action, its easy and complete removability, and still more by the fact that it has no reducing action on the titanic and platinic sulfates that are always present (in rock analysis);" and "Hydrogen sulfide is much more readily obtainable than sulfur dioxide—a minor, but practically important consideration."

<sup>8</sup> "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* 700, pp. 119-120.

<sup>9</sup> R. Fresenius, *Z. anal. Chem.*, 53, 595 (1914).

<sup>10</sup> Wilhelm Boller, "Beiträge zur titrimetrischen Bestimmung des Antimons, Zinns, Titans, Eisens und Urans," Zurich, 1915, p. 32.

<sup>11</sup> McBride, unpublished work carried on at the Bureau of Standards.

### III. Experimental.

Preliminary experiments demonstrated that compounds which were removed neither by filtration nor by prolonged boiling in a stream of carbon dioxide, and which subsequently reduced potassium permanganate, were formed in either hot or cold solutions: (1) when a dilute solution of sulfurous acid was treated with hydrogen sulfide; (2) when a freshly-prepared ammonium sulfide solution containing a very small amount of polysulfide was acidified with sulfuric acid; and (3) when a sulfuric acid solution of potassium permanganate was treated with hydrogen sulfide. That the reduction was not due to sulfur dioxide or hydrogen sulfide was demonstrated by the fact that aliquot portions of the solutions did not react with 0.1 *N* iodine solution.

It seemed entirely probable that similar reducing compounds would be formed in any reduction involving the use of hydrogen sulfide. Table I presents data which show the results that are to be expected in hydrogen sulfide reductions of iron carried out under varying conditions of acidity, volume of solution, temperature, and time of reduction.

Counterpoised weight burets were used throughout and corrections made in the usual manner for reagents and end-points. The iron solution was prepared from highest purity ferrous ammonium sulfate and its iron titer taken as an average of closely agreeing values found by reduction with sulfur dioxide, reduction in a Jones reductor, double gravimetric precipitations by ammonia with final correction for silica and precipitation with cupferron followed by silica correction. The permanganate solution was prepared with the necessary precautions and standardized by means of the Bureau of Standards sodium oxalate by the method of McBride.<sup>12</sup> The hydrogen sulfide used was passed through solutions of sodium hydrogen carbonate and blank runs demonstrated that it contained no products which subsequently consumed permanganate. Reductions were performed in glass wash-bottles in order that no organic material might be introduced.

All reduced iron solutions were tested with potassium thiocyanate and in Table I reductions were complete unless otherwise indicated. Since preliminary experiments demonstrated that sulfur alone in sulfuric acid solution was without effect on permanganate, titrations were performed in its presence unless otherwise specified.

A study of the data presented in Table I demonstrates that: (1) The hydrogen sulfide reduction method for iron ordinarily gives high values in completely reduced solutions. This holds true in all acidities, in reductions in cold or boiling solutions and in the presence or absence of sulfur. The high values are not in direct ratio to the quantity of iron

<sup>12</sup> McBride, *THIS JOURNAL*, 34, 393 (1912).

TABLE I.—DETERMINATION OF IRON BY ORDINARY HYDROGEN SULFIDE METHODS.

Iron.		Error. G.	Volume of solution. Cc.	H <sub>2</sub> SO <sub>4</sub> . % by volume.	Duration of H <sub>2</sub> S treatment in minutes.			CO <sub>2</sub> passed into boiling sol. Minutes.
Taken. G.	Found. G.				Cold.	Warming.	Boiling.	
0.0288	0.0295	+0.0007	200	0.2	0	0	60	60
0.0782	0.0799	+0.0017	350	0.6	95	0	0	"
0.1074	0.1099	+0.0025	300	0.6	30	15	60	60 <sup>b</sup>
0.1646	0.1673	+0.0027	200	0.8	0	0	60	60
0.1042	0.1054	+0.0012	100	1.0	0	0	70	60
0.0938	0.0980	+0.0042	250	1.0	0	0	75	60 <sup>c</sup>
0.1060	0.1075	+0.0015	350	2.0	20	15	45	60
0.0105	0.0108	+0.0003	100	2.5	30	15	30	60 <sup>d</sup>
0.1735	0.1741	+0.0006	100	2.5	30	15	30	60 <sup>d</sup>
0.0780	0.0786	+0.0006	350	2.5	120	0	0	"
0.0124	0.0130	+0.0006	300	2.5	30	15	30	30 <sup>f</sup>
0.1012	0.1027	+0.0015	350	3.0	20	15	60	60
0.1702	0.1733	+0.0031	300	5.0	30	15	0	30
0.1006	0.1018	+0.0012	350	5.0	20	15	60	60
0.00935	0.00955	+0.0002	100	5.0	30	15	0	30
0.0105	0.0113	+0.0008	100	5.0	40	25	0	30 <sup>f</sup>
0.1787	0.1794	+0.0007	100	5.0	40	25	0	30 <sup>f</sup>
0.0283	0.0280	-0.0003	100	5.0	15	15	0	30 <sup>g</sup>
0.1331	0.1335	+0.0004	100	5.0	15	15	0	30 <sup>h</sup>
0.0992	0.0881	-0.0111	350	7.5	0	15	60	60 <sup>g</sup>
0.1018	0.1003	-0.0015	350	7.5	30	25	0	60 <sup>g</sup>
0.1029	0.1031	+0.0002	350	8.0	20	15	55	60
0.0933	0.0936	+0.0003	350	10.0	20	15	60	60
0.0984	0.0969	-0.0015	350	10.0	20	15	60	60 <sup>i</sup>
0.0780	0.0733	-0.0047	100	10.0	120	0	0	i

<sup>a</sup> CO<sub>2</sub> passed into cold sol. for 100 min. and into boiling sol. 30 min.

<sup>b</sup> Titrated with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution. Sulfur filtered off before final reduction.

<sup>c</sup> Not reduced at end of 55 min., cooled in H<sub>2</sub>S for 10 min., and reboiled in H<sub>2</sub>S for 10 min.

<sup>d</sup> Sulfur filtered off before final reduction.

<sup>e</sup> CO<sub>2</sub> passed into cold sol. for 145 min. and into boiling soln. for 45 min.

<sup>f</sup> Sulfur filtered off before final reduction.

<sup>g</sup> Reduced sol. contained Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

<sup>h</sup> Reduced sol. contained no Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

<sup>i</sup> Reduced sol. contained Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

<sup>j</sup> CO<sub>2</sub> passed into cold sol. for 145 min. and into boiling sol. for 45 min. Reduced sol. contained Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

involved. (2) A low initial volume (100 cc.) and moderate acidity (2 to 2.5% by volume) is desirable. (3) Complete reduction in cold solution is slow, and in boiling solutions impossible in acidities much over 1%, especially in solutions of large volume. A favorable procedure consists in reduction in cold solution for 30 minutes, followed by warming to the boiling point for 15 minutes. (4) Complete reduction can sometimes be had

by the latter procedure in sulfuric acid concentrations as high as 10% by volume. Complete reduction in 5% by volume is easily attained.

Table II lists determinations carried out under the following conditions which were based for the most part on a study of the experiments listed in Table I: volume of solution, 100 cc.; acidity, 2.5% sulfuric acid by volume; hydrogen sulfide reduction 30 minutes in cold solution and 15 minutes as solution is heated to boiling; addition of 15 cc. of sulfuric acid (1:1); boiling for 30 to 60 minutes to a volume of approximately 50 cc. as a stream of carbon dioxide is bubbled through; cooling under the same conditions; dilution to 200 cc. with cold distilled water; and titration with standard permanganate solution. In some cases the separated sulfur was filtered off after the hydrogen sulfide treatment and after the reduced solution was cooled somewhat. The filtrate was then again treated with hydrogen sulfide for 10 minutes before proceeding as above described. The modified method differs from the method given by Hillebrand<sup>13</sup> in that the volume of the solution is fixed at 100 cc., the solution is not boiled as hydrogen sulfide is bubbled through and the acidity of the solution is raised before the expulsion of the hydrogen sulfide. The method differs from that advocated by McBride<sup>14</sup> in the latter two respects and also by the expressed limitation of the solution to small volume.

TABLE II.—DETERMINATION OF IRON BY THE MODIFIED HYDROGEN SULFIDE METHOD.

Iron.		Error.	CO <sub>2</sub> passed into the boiling sol. (minutes).	Remarks.
Taken.	Found.			
G.	G.	G.		
0.0129	0.0132	+0.0003	30	
0.1765	0.1766	+0.0001	30	Acidity at end of boiling was 25%.
0.00748	0.00756	+0.00008	60	Acidity at end of boiling was 33%.
0.0266	0.0267	+0.0001	60	Acidity at end of boiling was 33%.
0.1253	0.1253	0.0000	50	Sulfur filtered off before final
0.00442	0.00455	+0.00013	60	reduction.
				Sulfur filtered off before final
0.0254	0.0256	+0.0002	60	reduction.
				Sulfur filtered off before final
0.1310	0.1313	+0.0003	60	reduction.

The data in Table II demonstrate that while the modified method still gives values which are slightly high, determinations by the method are sufficiently accurate for most purposes. Incidentally, it is seen that ferrous sulfate is not oxidized upon boiling in a solution containing 33% (by volume) of sulfuric acid. The authors did not carry out experiments

<sup>13</sup> Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* 700, pp. 119-20.

<sup>14</sup> Unpublished.

dealing with slight variations of the modified method on account of the ease with which the specified conditions can be met.

Table III presents data obtained in the determination of vanadium by the ordinary hydrogen sulfide reduction and also by the modified method. The vanadium solution was standardized by sulfur dioxide reduction and also by reduction in a Jones reductor with ferric alum and phosphoric acid in the receiver.

TABLE III.—DETERMINATION OF VANADIUM BY THE ORDINARY AND BY THE MODIFIED HYDROGEN SULFIDE METHOD.

Vanadium.					
Taken. G.	Found. G.	Error. G.	Volume of solution cc.	H <sub>2</sub> SO <sub>4</sub> (% by Volume).	Remarks.
0.0469	0.0482	+0.0013	250	0.5	Ordinary Method.
0.0419	0.0428	+0.0009	250	0.5	Ditto, sulfur filtered off.
0.0430	0.0431	+0.0001	100	2.5	Modified Method.
0.0469	0.0469	0.0000	100	2.5	Ditto.

It is apparent that high results are to be expected in ordinary hydrogen sulfide reductions of vanadium and that satisfactory values are obtained with the modified method. Hillebrand<sup>15</sup> has noted the former and states "One or two checks (on vanadium) are always to be made by reducing again (after titration of the solution reduced by hydrogen sulfide) by means of a current of sulfur dioxide, boiling this out again and repeating the titration. The latter results are apt to be a very little lower than the first and are to be taken as the correct ones." The higher value in the first titration was ascribed by Hillebrand to the extraction of oxidizable matter from the filter paper used to filter off sulfur and sulfides, as noted by McBride and Scherrer,<sup>16</sup> and recently, under more severe conditions, by Myhill.<sup>17</sup>

As sulfur alone is without effect on permanganate and the sulfur in Expt. 2 was filtered off on a filter paper freshly washed with acid it is certain that the higher values cannot be ascribed entirely to oxidizable extracts from filter papers.

#### IV. Conclusions.

Published methods for the reduction of iron by hydrogen sulfide are faulty in either of two respects: (1) complete reduction is impossible or, (2) when reduction is complete, other oxidizable compounds are formed

<sup>15</sup> *Op. cit.*, p. 188.

<sup>16</sup> McBride and Scherrer, *THIS JOURNAL*, 39, 928 (1917).

<sup>17</sup> Myhill, *Chem. Age*, 4, 151 (1921).



which cause high values.<sup>18</sup> The second statement also applies to the determination of vanadium.

The hydrogen sulfide method for iron or vanadium as herein modified is sufficiently accurate for all ordinary work.

In case the highest accuracy is desired, the sulfur dioxide method is recommended. Sulfur dioxide reduces vanadium to the quadrivalent condition and does not reduce quadrivalent titanium. Unfortunately it reduces platinum to the bivalent condition and also reduces various members of the hydrogen sulfide group; consequently when platinum (as is usually the case in rock analysis, owing to the platinum ware employed) or other members of the hydrogen sulfide group are present, a modification of the method already used in the determination of vanadium by Hillebrand<sup>19</sup> is called for, namely, precipitation with hydrogen sulfide in acid solution, separation of sulfides by filtration, boiling out of hydrogen sulfide in the filtrate, complete oxidation by 10% permanganate solution and final reduction with sulfur dioxide gas. The following notes and precautions, taken for the most part from the work of Hillebrand<sup>20</sup> are of interest in the later operation.

The direct use of a solution of sulfur dioxide or of an alkali sulfite is inadmissible unless these have been freshly prepared, for after a lapse of time they contain other oxidizable bodies than sulfurous acid or a sulfite.

Sulfur dioxide is most conveniently obtained from a cylinder of the liquefied gas or, in default of this, by heating a flask containing a solution of sulfur dioxide, or of a sulfite to which sulfuric acid has been added.

Reductions with this gas require low initial acidities, and hydrochloric acid—chloride solutions are reduced more rapidly than sulfuric acid—sulfate solutions; in the former case a titration with permanganate requires previous addition of titrating solution as in the Zimmermann-Reinhardt method.

Reduced solutions containing sulfur dioxide should not be allowed to stand for over 24 hours lest other oxidizable bodies be formed.

The expulsion of the last trace of sulfur dioxide is said to be accomplished more effectively by boiling with simultaneous passage of a rapid current of carbon dioxide.

The authors have not made any serious attempts to isolate and identify the oxidizable compound or compounds which are formed in hydrogen

<sup>18</sup> It is to be borne in mind that these oxidizable compounds are quite stable and consequently may cause trouble in any quantitative operation calling for a final oxidation as, for instance, where the hydrogen sulfide solution is boiled to expel the gas and then reduced by stannous chloride or in a Jones reductor preliminary to titration with dichromate or permanganate. The obvious remedy lies in complete oxidation before the final reduction.

<sup>19</sup> Hillebrand, *op. cit.*, p. 168.

<sup>20</sup> Hillebrand, *ibid.*, p. 186.

sulfide reductions. It is believed that they are polythionic acids and it has been noted that (1) they are quite stable upon boiling with sulfuric acid in concentrations as high as 33% by volume; (2) they are volatile upon prolonged boiling; (3) the volatilized compounds do not react with iodine solution; and (4) their dilute solutions give with silver nitrate solution a yellowish-brown coloration.

### V. Summary.

1. The determination of iron or of vanadium by reduction with hydrogen sulfide followed by titration with permanganate or dichromate ordinarily gives high values.

2. These high values are not due to the presence of sulfur and persist in spite of the complete expulsion of hydrogen sulfide and the avoidance of organic matter extracted from filter paper. They may be ascribed to polythionic acids which are not destroyed by boiling in moderately conc. sulfuric acid solution and which are volatilized slowly from dilute and more rapidly from concentrated solutions.

3. Reasonably accurate determinations may be made by restricting the original solution to 100 cc. and proceeding by the described modified method.

4. For accurate determinations of iron and vanadium in solutions containing platinum (as in rock analysis) a preliminary separation of the hydrogen sulfide group, followed by expulsion of the gas, complete oxidation with permanganate and reduction with sulfur dioxide is recommended.

The authors desire to express to Dr. W. F. Hillebrand their sincere appreciation of his aid and counsel.

WASHINGTON, D. C.

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(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY,  
No. I, 6.)

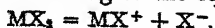
## THE CONDUCTANCE OF SOLUTIONS OF TERNARY ELECTROLYTES IN PROPYL ALCOHOL.

BY CHARLES A. KRAUS AND JOHN EGBERT BISHOP.

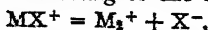
Received March 30, 1921.

### I. Introduction.

Our knowledge of the ionization process of ternary electrolytes in non-aqueous solvents is very limited and even in the case of aqueous solutions the nature of the ionization process for these substances is uncertain. If intermediate ions are formed according to the equation



which, in turn, break down according to the equation



then it is not possible to determine the equilibrium in the solution by means

of conductance measurements alone. In view of the fact that the laws governing solutions of strong electrolytes are not known, other properties of these solutions cannot be employed to supply the additional relation necessary to obtain a solution of the problem. In the case of weak acids and bases it has been shown that intermediate ions are formed. Noyes and Eastman<sup>1</sup> have established that a similar process takes place in solutions of sulfuric acid. In the case of salts, however, no definite evidence exists to show that intermediate ions are formed, although Harkins,<sup>2</sup> from the effect of various electrolytes upon the solubility of difficultly soluble salts of higher type, has reached the conclusion that intermediate ions do, in fact, exist.

Schlamp<sup>3</sup> measured the conductances of solutions of sodium iodide, lithium chloride and calcium chloride in propyl alcohol. Völlmer<sup>4</sup> drew from Schlamp's results the conclusion that calcium chloride behaves like a binary electrolyte in propyl alcohol solution, its conductance curve lying intermediate between those for lithium chloride and sodium iodide and being approximately parallel to them. It seemed worth while to measure the ionization of a number of ternary electrolytes in propyl alcohol in order to determine whether Schlamp's results and Völlmer's conclusions therefrom could be substantiated. Incidentally, it may be stated that, in fact, Schlamp's values for the conductance of calcium chloride solutions lie below those for lithium chloride and sodium iodide and not between them.

## II. Apparatus and Materials.

The conductance cell employed consisted of a cylindrical tube about 40 cm. long, having a capacity of approximately 200 cc. It was provided with platinized electrodes at the bottom and with a neck and a ground-glass stopper at the top. This neck was bent at an angle of 60° with the axis of the cell in order to facilitate the process of mixing the solutions.

The cell constant was determined by means of 0.02 *N* and 0.01 *N* solutions of potassium chloride, whose specific conductance values at these concentrations were assumed to be 0.002397 and 0.001225 respectively. The constant of the cell was determined to be 0.2049 at 18.00°.

Propyl alcohol was prepared by repeated fractionation and was finally dehydrated by means of metallic sodium. Immediately before introducing into the cell, a small amount of sodium was added to the alcohol. It was then distilled directly into the conductance cell, the intermediate fraction only being used. The specific conductance of the pure solvent varied between  $1.3$  and  $1.7 \times 10^{-7}$ . The value of the specific conductance of the solvent was in each case subtracted from that of the solution, the differ-

<sup>1</sup> Noyes and Eastman, "Electrical Conductivity of Aqueous Solutions," *Carnegie Inst. Pub.*, No. 63, p. 239 (1907).

<sup>2</sup> Harkins, *THIS JOURNAL*, 33, 1836 (1911).

<sup>3</sup> Schlamp, *Z. physik. Chem.*, 14, 272 (1894).

<sup>4</sup> Völlmer, *Ann. Physik.*, 22, 328 (1894).

ence being assumed to give the true value for the specific conductance of the electrolyte in solution.

The salts employed were anhydrous calcium nitrate and the hexahydrate of magnesium nitrate. The calcium nitrate was imported c. p. material and was further purified by two crystallizations from doubly distilled water and finally from conductivity water. Contrary to the statement made in Abegg's "*Handbuch der Anorganischen Chemie*," it was not found possible to dehydrate the crystallized salt at 160° in air. At the end of 3 days, so much water of crystallization remained that the entire mass was still completely liquid. The salt was then placed in a desiccator over phosphorus pentoxide which was then evacuated to a pressure as low as 0.001 mm. At the end of 5 days an appreciable amount of water still remained in the salt. It was then placed in one arm of an H-tube, the other arm of which was filled with phosphorus pentoxide. A plug of glass wool was placed between the two arms to prevent contamination of the salt. The tube was exhausted to a pressure below 0.001 mm. and sealed off. The limb containing the salt was then heated for 2.5 days in a water-bath at 100°; that containing the phosphorus pentoxide remaining at room temperature. At the end of that time no trace of water could be found.

The magnesium nitrate was an imported grade "For Analysis" and no further purification was attempted. It was at first intended to dehydrate this salt also, but the attempt was abandoned since, after treating for 4 days at 100° with phosphorus pentoxide in a high vacuum, a considerable amount of water was still left in the salt. As the crystallized salt is quite hygroscopic, the excess of moisture was removed by placing it in a tube and passing over it a current of air which had previously been passed through 3 ordinary potash bulbs filled with 40 % sulfuric acid, and thereafter filtered. Although the vapor pressure of sulfuric acid at this concentration is considerably above that given for  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at 20°, it was considered advisable to make a determination of the actual magnesium content of the salt. It was found that the salt contained 1.01 % of magnesium in excess of that corresponding to the above formula. This correction has been applied to the calculations.

Anhydrous barium nitrate was also prepared but could not be employed, as it was found to be only slightly soluble in the anhydrous alcohol. Strontium nitrate and strontium and barium chlorides were likewise found to be only slightly soluble, the last named salt being somewhat more soluble than the others.

The alcohol content of the cell was obtained by weighing. Because of the small amount of salt required for the more dilute solutions, these were made up by introducing into the cell a weighed quantity of a more concentrated solution. This solution was weighed in a small pipet, somewhat similar to an Ostwald pycnometer. The outlet tube was protected by means of a cap covering the end of the capillary and the other tube by means of a stopcock. This method of making up the solutions was employed in all cases, except that of calcium nitrate, where the last three concentrations were made by weighing the salt directly. Since the concentration never exceeded 0.1 normal, it was assumed that the density of the solutions is equal to that of the pure solvent, whose density is 0.8043 at 18°.

### III. Experimental Results.

The results are given in the following table, in which the weight  $W$  of the concentrated solution added is given in the first column, the concentration

of the salt in millimols per liter is given in the second column, the molecular conductance  $\Lambda$ , corrected for the specific conductance of the solvent, in the third column, and the logarithm of the dilution  $V$  in the last column. At the head of the table the initial weight of the solvent is given under  $W_0$ , the specific conductance of the pure solvent under  $l_0$ , and the concentration of the added solution under  $C_s$ .

TABLE I.—CONDUCTANCE OF ANHYDROUS CALCIUM NITRATE IN ANHYDROUS PROPYL ALCOHOL AT 18.00°.

$W_0 = 141.075.$	$l_s = 1.7 \times 10^{-7}.$	$C_s = 0.008922.$	
$W.$	$C \times 10^3.$	$\Delta.$	$\text{Log } V.$
1.1780	0.363	5.140	3.4413
2.6023	0.792	3.834	3.1013
5.4169	1.617	2.894	2.7913
11.597	3.326	2.184	2.4781
22.006	5.908	1.798	2.2286
28.004	7.247	1.688	2.1398
0.4943	14.320	1.258	1.8441
0.8645	24.930	0.976	1.6033
1.4724	43.290	0.722	1.3636

To the most concentrated solutions was added 0.5795 g. of water. The concentration of the resulting solution was  $43.27 \times 10^{-3}$  mols per liter and its molecular conductance 2.036. On the further addition of 0.5023 g. of water to the same solution, the molecular conductance was raised to 2.991 at a concentration of  $43.25 \times 10^{-3}$  mols per liter.

The conductance values for magnesium hexahydrate in anhydrous propyl alcohol are given in Table II.

TABLE II.—CONDUCTANCE OF MAGNESIUM NITRATE HEXAHYDRATE IN ANHYDROUS PROPYL ALCOHOL AT 18.00°.

$W_0 = 93.005.$	$l_0 = 1.53 \times 10^{-7}$	$C_s = 0.055941.$
$W.$	$C \times 10^4.$	$\Lambda.$
		$\text{Log } V.$
0.2128	394	12.422
0.4672	865	10.730
1.0579	1942	8.932
1.9588	3483	7.774
3.5808	6406	6.408
6.2129	9804	6.026
12.757	1989	4.674
25.324	3612	3.866

In Table III are given the conductance values for magnesium nitrate hexahydrate in a mixture of propyl alcohol and water, containing 95.77 g. of propyl alcohol and 0.632 g. of water.

TABLE III.—CONDUCTANCE OF MAGNESIUM NITRATE HEXAHYDRATE IN A MIXTURE OF PROPYL ALCOHOL AND WATER.

$W_c = \begin{cases} 95.77 \text{ g. } C_3H_7OH \\ 0.632 \text{ g. } H_2O. \end{cases}$		$I_s = 3.45 \times 10^{-7}.$	$C_s = 0.08822.$	
$W.$	$C \times 10^6.$	$\Lambda.$	$\log V.$	
0.1044	298	17.774	3.5258	
0.6879	1950	9.062	2.7100	
1.3343	3758	7.326	2.4260	
2.3173	6339	6.188	2.1980	
4.2936	11670	5.096	1.9329	
7.376	19460	4.400	1.7009	
12.019	30410	3.921	1.5170	
21.210	49560	3.554	1.3049	

## IV. Discussion of Results.

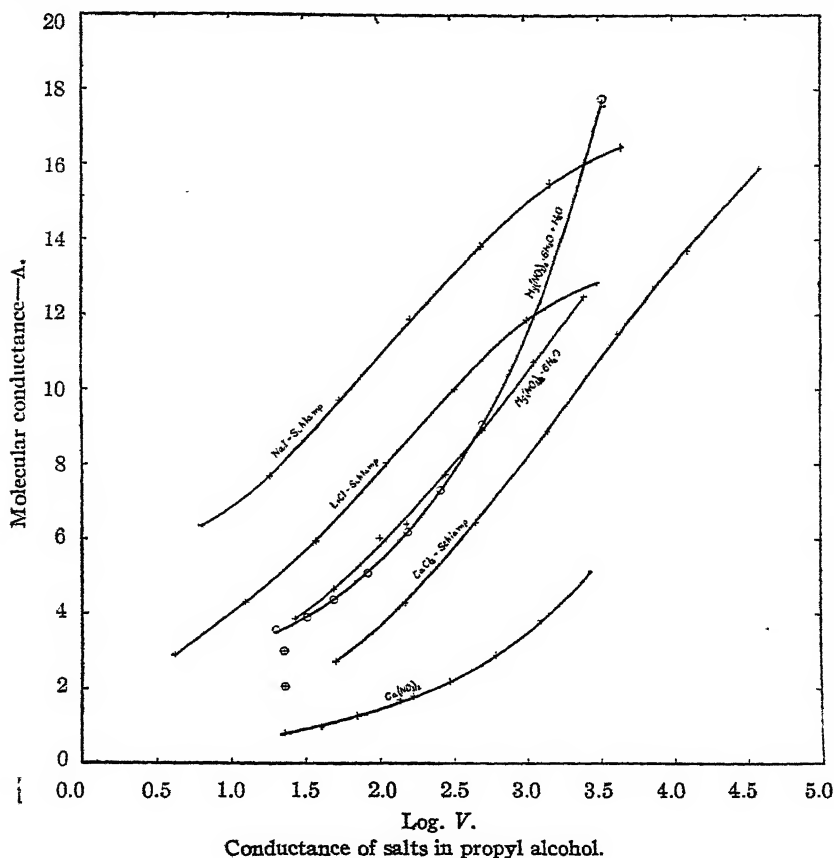
The results are shown graphically in the accompanying figure, values of  $\log V$  being plotted as abscissas and those of  $\Lambda$ , the molecular conductance, as ordinates. The nature of the electrolyte and the solvent is in each case shown on the figure. In the same figure are shown the conductance curves for sodium iodide, lithium chloride, and calcium chloride, obtained by Schlamp. Since calcium chloride, calcium nitrate, and magnesium nitrate are ternary salts, their molecular conductance, if ionization is anywhere near complete, should be approximately twice that of a binary electrolyte; while, if they ionized according to Equation I, their molecular conductance should be very nearly the same as that of binary electrolytes, the concentration, of course, being expressed in mols per liter.

It is evident from an examination of the curves that Völlmer's conclusion that calcium chloride ionizes according to a binary process is not justified. Schlamp's conductance curve for calcium chloride lies much below that for both lithium chloride and sodium iodide. Moreover, the curve for calcium chloride does not run parallel to that of the curves of the binary salts.

Another uncertainty in Schlamp's results lies in the fact that he has not specified the condition of his calcium chloride. This salt crystallizes as a hexahydrate and is dehydrated with great difficulty. Since he makes no mention of any facts in this connection, it is probable that he employed the hydrated salt. It is also probable that Schlamp's alcohol was not completely free from water, since he dehydrated it only with fused potassium carbonate. The presence of small amounts of water has a great influence upon the conductance curve of electrolytes which exhibit a marked tendency to form compounds containing water of crystallization.

Schlamp's curve for calcium chloride resembles that for the hydrated magnesium nitrate in anhydrous propyl alcohol. The conductance values for the hydrated salts in anhydrous propyl alcohol are relatively low at the

higher concentration and increase markedly at lower concentrations. There is no indication that these curves are approaching a limiting value as



the concentration decreases, and it must therefore be assumed that ions of the type  $\text{M}^{++}$  are present.

No previous data are available on the influence of small additions of water upon the conductance of ternary electrolytes in non-aqueous solutions. In general, the conductance of ternary electrolytes in anhydrous solvents is relatively low. That the ionization is generally increased by the addition of water may be concluded from the work of Jones and his co-workers, who have measured the conductance of a considerable number of mixtures containing 25% of water. It is evident that the initial additions of water cause a large increase in the conductance of the solutions. The addition of 3.62% of water raises the molecular conductance of calcium nitrate from 0.772 to 2.036, or 2.64 times; while the addition of 6.75% raises it to 2.991, or 3.88 times the value in the anhydrous solvent. These

points are represented in the figure by  $\oplus$  at the concentration  $\log V = 1.36$ . A comparison of the conductance curves for magnesium nitrate hexahydrate in dry alcohol and in the presence of approximately 0.7% of water likewise clearly shows the influence of water upon the conductance of the solutions. The two curves intersect at two points. At low concentrations the additions of water cause a marked increase in the conductance of the solution, while at intermediate concentrations the addition of water causes a slight decrease in the conductance of the solution. It is to be presumed that at considerably higher concentrations the addition of water would cause a relatively large increase in the conductance of the solution. It is probable that the curve for anhydrous magnesium nitrate does not differ measurably from that for calcium nitrate. The diminution in the conductance due to the addition of water at intermediate concentrations of salt is probably due to the fact that on addition of larger amounts of water the ionic complexes formed have a relatively lower speed than those which contain less water. Somewhat similar results are obtained on the addition of water to solutions of acids.<sup>5</sup> When small amounts of water are added to solutions of strong acids in alcohol, the equivalent conductance of the acid is greatly reduced. This reduction appears to be due to the formation of a complex hydrogen ion whose speed is relatively low. It is interesting to note that on the addition of water to weak acids the conductance is increased and this increase is in general the greater the weaker the acid. This increase is apparently due to an increase in the ionization of the dissolved electrolyte, due to the addition of water. Lithium chloride in ethyl alcohol also shows a slight increase on addition of water. This influence of water upon the conductance of solutions of electrolytes which show a marked tendency to form complexes with water, is readily accounted for on the assumption that the ionization of the complex formed is greater than that of the non-hydrated electrolyte. This is in excellent agreement with Werner's theory of the constitution of salts.

## V. Summary of Results.

1. The conductance of an anhydrous ternary salt in anhydrous propyl alcohol has been measured.
2. The effect of the addition of varying amounts of water to solutions of anhydrous ternary electrolytes in anhydrous propyl alcohol has been studied.
3. A comparison of the results of the present investigation with those of Schlamp indicates that he employed hydrated calcium chloride.

<sup>5</sup> Goldschmidt, *Z. physik. Chem.*, 89, 129 (1915).



4. A critical examination of the results obtained by Schlamp lends no support to the view that ternary salts in this solvent ionize according to a binary process.

WORCESTER, MASS.

[CONTRIBUTION FROM THE BUREAU OF SOILS AND THE FIXED NITROGEN RESEARCH  
LABORATORY.]

## VAPOR PRESSURE OF LITHIUM NITRATE:AMMONIA SYSTEM.<sup>1</sup>

By R. O. E. DAVIS, L. B. OLMSTEAD AND F. O. LUNDSTRUM.

Received April 4, 1921.

In recent work on the absorption of ammonia from a mixture of hydrogen and nitrogen gases used in ammonia synthesis the desirability of employing as absorbent some substance other than water became evident. A number of good absorbents for ammonia are known, but each has its disadvantages for our purpose. Liquid absorbents seem more desirable than solid but only two other than water which meet most of the requirements have been mentioned in the literature. The desirable qualities in an absorbing liquid are that its water vapor pressure be low over a considerable range in temperature and that the vapor pressure of ammonia vary considerably over a short range in temperature. The liquid should be non-corrosive to ordinary metals so that it can be used as a circulating medium and should not cause any obstruction in the pipes, valves, or other parts of the system.

Solid ammonium nitrate treated with anhydrous ammonia liquefies, giving a liquid rich in ammonia and remaining liquid over considerable range in temperature. This is the well known Divers Solution<sup>2</sup> and has been studied by Kuriloff.<sup>3</sup> Similarly, ammonium thiocyanate forms a liquid with ammonia as first noted by Bradley and Alexander<sup>4</sup> and this has been studied by Foote and Hunter,<sup>5</sup> who have shown some of the desirable properties of this liquid for the purpose we have in mind; namely, the removal of ammonia from a mixture of gases and its subsequent recovery free from these gases. However, a serious draw-back to the use of these liquids is that they attack metals rapidly.

In searching for a suitable liquid absorbent we have investigated substances listed by Franklin and Kraus,<sup>6</sup> as very easily soluble, easily soluble, and miscible in liquid ammonia. A number of these were eliminated as undesirable for our purpose merely by inspection, but quite a number

<sup>1</sup> Published by permission of the Chief of Ordnance, U. S. Army.

<sup>2</sup> *Chem. News*, 27, 37.

<sup>3</sup> Kuriloff, *Z. physik. Chem.*, 25, 107 (1898).

<sup>4</sup> Alexander, *THIS JOURNAL*, 34, 15 (1914).

<sup>5</sup> Foote and Hunter, *ibid.*, 42, 69 (1920).

<sup>6</sup> Franklin and Kraus, *Am. Chem. J.*, 20, 820.

were tested to determine whether, as with ammonium nitrate, a liquid formed on treatment of the solid with anhydrous ammonia gas. In carrying out these tests 10 g. of the substance was placed in an absorbing bottle and a stream of dried ammonia gas from a liquid ammonia cylinder was passed through the bottle. If evidences of liquefaction were shown after 10 or 15 minutes' treatment this was continued until the entire mass became liquid or no further change was observed in the material. If no change was observed a small amount of water was added and ammonia was passed through again. In some cases small amounts of moisture did cause liquefaction of the mass with high absorption of ammonia. One cc. of the liquid thus obtained was titrated with a standard sulfuric acid solution to determine roughly the amount of ammonia absorbed. The following substances shown in Table I were tested with positive results.

TABLE I.

Subs.	On addition of $\text{NH}_3$ .	Water added. Cc.	1 cc. of sol. at $24^\circ$ neut'd 0.95 N $\text{H}_2\text{SO}_4$ Cc.	Remarks.
$\text{NH}_4\text{I}$	Insoluble	10	14.1	
$\text{NH}_4\text{Br}$	Insoluble	15	15.9	
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Soluble	5	18.5	Viscous at $24^\circ$
$\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	Sludge formed	3	19.2	White suspension
$\text{NaNO}_2$	Insoluble	12	14.7	Not completely sol.
$\text{KNO}_3$	Insoluble	10	12.0	Not very sol. with $\text{H}_2\text{O}$
$\text{Pb}(\text{NO}_3)_2$	Insoluble	Insol.		
$\text{LiNO}_3$	Soluble		26.0	Slightly cloudy
$\text{HgNO}_3$	Pasty mass	Insol.		
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Deliquesces	Insol.		Color change yellow to orange
$\text{Cu}(\text{NO}_3)_2$	Pasty mass	10	14	Color change blue to indigo
$\text{NH}_4\text{Cl}$	Insoluble	10	14	Partly soluble
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	Soft mass	10		$\text{H}_2\text{O}$ gave no further action
$\text{KI}$	Insoluble	10	15.8	
$\text{NaI}$	Partly soluble	3	19.2	Suspension
$\text{NaBr}$	Insoluble	9	16.0	
$\text{AgNO}_3$	Pasty then solid	10	15.0	
Lactose	Insoluble	10	13.4	
$\text{Sr}(\text{NO}_3)_2$	Insoluble	6	10.4	

Of the substances thus tested, lithium nitrate appears to have the highest absorptive value, and hence we have determined the total vapor pressure of seven solutions of lithium nitrate in pure and aqueous ammonia.

These solutions were prepared by saturating c. p. recrystallized lithium nitrate with ammonia at different temperatures. The method used for determining the vapor pressure was a static one, and the apparatus is shown in Fig. 1. The solution was introduced into a bulb connected to a manometer and placed in a thermostat. Stirring

was accomplished by an electromagnetic arrangement consisting of a small plate of sheet platinum attached to a platinum wire carrying on its upper end an iron nail coated

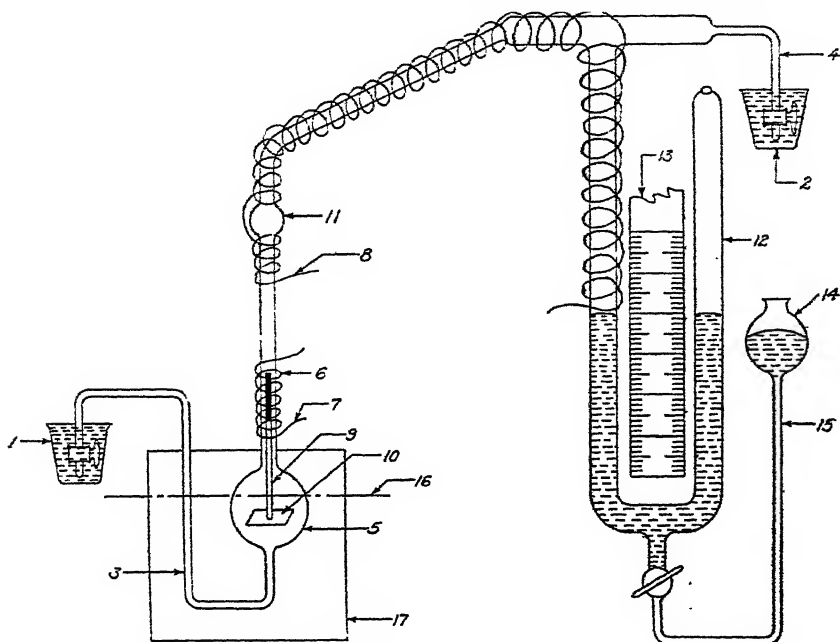
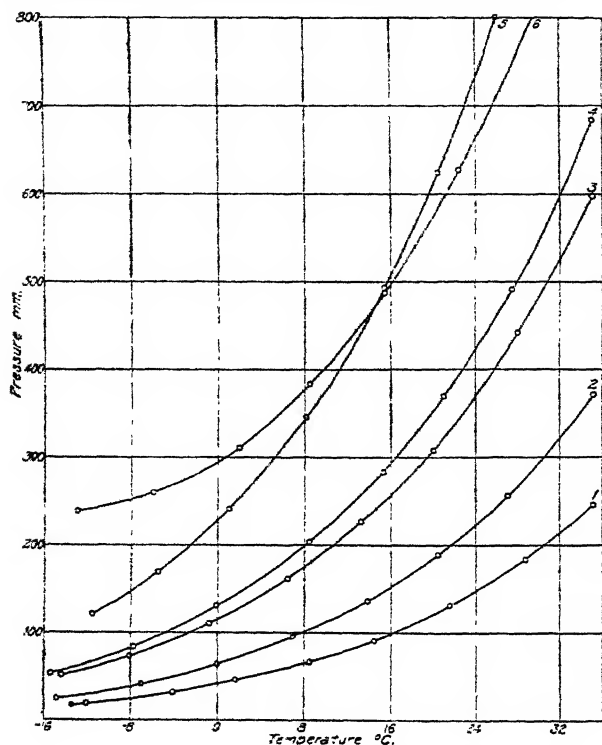


Fig. 1.—Vapor pressure apparatus; Nos. 1 and 2, mercury seals; Nos. 3 and 4, capillary tubes and cocks; No. 5, glass bulb; No. 6, iron nail (coated with glass); No. 7, solenoid; No. 8, heating wire; No. 9, glass rod; No. 10, platinum foil and wire; No. 11, safety bulb; No. 12, glass manometer; No. 13, meter stick; No. 14, mercury leveling bulb; No. 15, rubber capillary tube; No. 16, liquid level; No. 17, thermostat.

with glass, to prevent corrosion. Movement of the stirrer was accomplished by interrupted current through a solenoid on the outside of the glass tubing just about the height of the upper end of the iron nail. Other features of the apparatus require no special description. Samples of the material used were drawn off through a capillary for analysis for ammonia and for nitrates.

The range of the measurements was from  $-14^{\circ}$  to  $35^{\circ}$ , and the results of these measurements are shown in Fig. 2.

An inspection of the curves shows that lithium nitrate is very soluble in ammonia and that the vapor pressure of the ammonia is very much lowered by the presence of the dissolved salt. The curve is somewhat flatter where water is present and becomes steeper with an increase of ammonia. The curve for lithium nitrate containing no water shows a low vapor pressure of ammonia at  $0^{\circ}$ , and a pressure exceeding an atmosphere at  $35^{\circ}$ , thus giving a rather wide variation of pressure over a comparatively short range in temperature.

Fig. 2.—Vapor pressure of  $\text{NH}_3:\text{LiNO}_3$  solutions.

1 {	17.98% $\text{NH}_3$	2 {	21.5% $\text{NH}_3$	3 {	23.3% $\text{NH}_3$
	45.72% $\text{LiNO}_3$		42.25% $\text{LiNO}_3$		18.04% $\text{LiNO}_3$
	36.30% $\text{H}_2\text{O}$		36.25% $\text{H}_2\text{O}$		58.66% $\text{H}_2\text{O}$
4 {	26.2% $\text{NH}_3$	5 {	38.43% $\text{NH}_3$	6 {	36.34% $\text{NH}_3$
	30.07% $\text{LiNO}_3$		55.51% $\text{LiNO}_3$		63.66% $\text{LiNO}_3$
	43.73% $\text{H}_2\text{O}$		6.06% $\text{H}_2\text{O}$		

TABLE II.

 $\text{NH}_3:\text{LiNO}_3:\text{H}_2\text{O}$ . $\text{NH}_3, 17.98\%; \text{LiNO}_3, 45.72\%; \text{H}_2\text{O}, 36.30\%.$ 

Temp. °C.	Pressure mm.
-13.5	16.7
-12.15	19.64
-4.15	31.9
1.67	46.27
8.47	66.77
14.42	91.14
21.56	131.0
28.65	183.2
35.17	246.85

TABLE III.

 $\text{NH}_3:\text{LiNO}_3:\text{H}_2\text{O}$ . $\text{NH}_3, 21.5\%; \text{LiNO}_3, 42.25\%; \text{H}_2\text{O}, 36.25\%.$ 

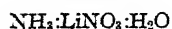
Temp. °C.	Pressure mm.
-14.85	24.54
-6.97	41.60
0.03	63.8
7.00	95.31
13.95	136.4
20.4	188.39
27.05	256.98
35.2	371.1
.....	.....

TABLE IV.

 $\text{NH}_3, 23.3\%; \text{LiNO}_3, 18.04\%; \text{H}_2\text{O}, 58.66\%.$ 

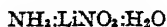
Temp. °C.	Pressure mm.
-14.45	50.82
-8.10	73.7
0.75	110.2
6.45	161.9
13.35	225.23
20.00	307.97
28.00	441.75
35.10	598.09

TABLE V.

 $\text{NH}_3, 26.2\%; \text{LiNO}_3, 30.07\%; \text{H}_2\text{O}, 43.73\%.$ 

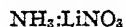
Temp. °C.	Pressure mm.
-15.4	52.86
-7.8	84.35
-0.10	131.81
8.4	203.09
15.23	283.43
21.00	369.72
27.5	491.54
35.1	683.10

TABLE VI.

 $\text{NH}_3, 38.43\%; \text{LiNO}_3, 55.51\%; \text{H}_2\text{O}, 6.06\%.$ 

Temp. °C.	Pressure mm.
-11.6	121.34
-5.5	169.64
1.03	242.08
8.17	345.39
15.39	493.04
20.45	623.82
27.57	862.74
34.4	1140.92

TABLE VII.

 $\text{NH}_3, 36.34\%; \text{LiNO}_3, 63.66\%.$ 

Temp. °C.	Pressure mm.
-13.0	239.32
-6.02	259.94
1.53	321.90
8.48	382.9
15.5	487.45
22.4	627.39
30.05	818.13
35.00	998.16

Solid  
phase.

## Action on Metals.

Solutions of lithium nitrate in pure and aqueous ammonia were tested as to their action upon certain metals. After remaining in contact with machine steel and iron wire for several months no appreciable action had taken place. Nichrome wire placed in such solutions was not attacked but a nickel-steel alloy showed slight action after many months.

## Use of Solution.

It appears from these results that a solution of lithium nitrate in liquid ammonia with a small addition of water would possess desirable quantities for the removal of ammonia from a mixture of gases such as hydrogen, nitrogen, and ammonia. The absorption could be carried out at a temperature around  $0^\circ$ , or somewhat lower and a large portion of ammonia released either by a comparatively small increase in temperature or by reduction in pressure. The presence of water vapor would not have to be considered if this were an undesirable constituent of the gas leaving the absorbing medium. One of the very desirable properties is that ordinary steel or iron could be used in the construction of apparatus for absorption of ammonia and for circulation of the liquid.

## Summary.

1. A number of substances have been found to liquefy when treated with anhydrous ammonia gas or on the addition of small amounts of water.

2. The total vapor pressures of several mixtures of lithium nitrate, ammonia and water have been measured.

3. The lithium nitrate-ammonia solution could be used as an absorbent for ammonia, as in the synthetic process.

4. The corrosive action of such a solution on ordinary iron or steel is not appreciable after several months' contact.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE BUREAU OF SOILS AND THE FIXED NITROGEN RESEARCH LABORATORY.]

VAPOR PRESSURE OF AMMONIA-SALT SOLUTIONS.<sup>1</sup>

By R. O. E. DAVIS, L. B. OLMSTEAD AND F. O. LUNDSTRUM.

Received April 4, 1921.

The work leading up to the study of lithium<sup>2</sup> nitrate:ammonia system also led us to consider calcium nitrate; sodium iodide; calcium chloride; ammonia nitrate; and ammonium thiocyanate:ammonia solutions. Ordinary crystalline calcium nitrate with four molecules of water forms a liquid with anhydrous ammonia gas, which is rather viscous at 24°. With the addition of water this solution becomes less viscous and offers the hope of meeting the requirements of an absorbent liquid. The measurements of vapor pressure were carried out in the same apparatus as used in the lithium nitrate experiments. The vapor pressures of two solutions of calcium nitrate, one of which contains 58.34% of water and the other

TABLE I (Curve 1).

$\text{NH}_3:\text{Ca}(\text{NO}_3)_2:\text{H}_2\text{O}$   
 $\text{NH}_3, 19.18\%; \text{Ca}(\text{NO}_3)_2,$   
 $22.48\%; \text{H}_2\text{O}, 58.34\%.$

Temp °C.	Pressure mm.
-14.5	34.8
-9.3	48.1
-2.2	73.2
5.3	110.2
15.1	181.7
21.15	242.0
29.5	354.0
36.35	474.0

TABLE II (Curve 2).

$\text{NaI}:\text{NH}_3:\text{H}_2\text{O}$   
 $\text{NH}_3, 16.06\%; \text{NaI},$   
 $32.34\%; \text{H}_2\text{O}, 51.60\%.$

Temp. °C.	Pressure mm.
-14.4	40.9
-8.0	61.14
-1.2	90.4
3.15	116.3
10.7	170.8
17.9	242.4
25.8	347.5
35.0	519.2

<sup>1</sup> Published by permission of the Chief of Ordnance, U. S. Army.

<sup>2</sup> See preceding article by the authors.

18.43% of water, were determined. These are shown in Curves 1 and 6, Fig. 1, and Tables I and VI. It may be seen that these solutions have qualities similar to those of lithium nitrate although the amount of am-

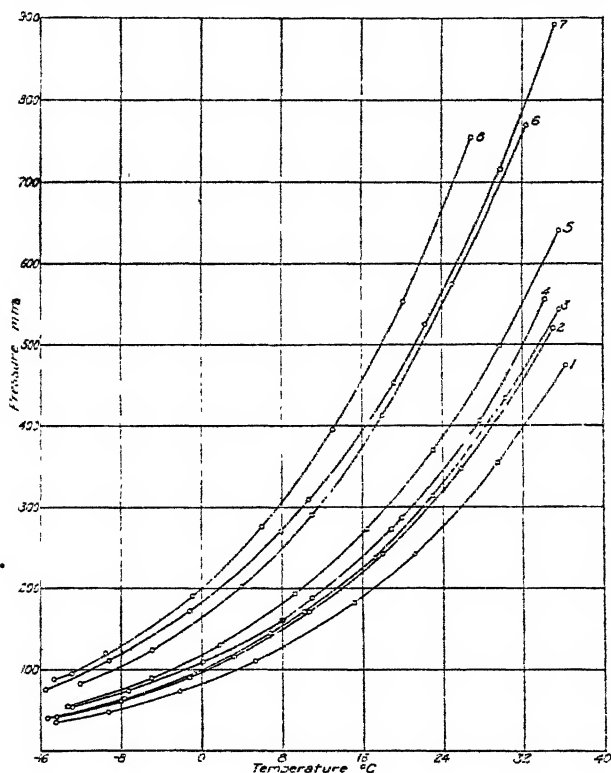


Fig. 1.—Vapor pressure of ammonia-salt solutions.

1 { 22.48% $\text{Ca}(\text{NO}_3)_2$ 19.18% $\text{NH}_3$ 58.34% $\text{H}_2\text{O}$	2 { 32.34% $\text{NaI}$ 16.06% $\text{NH}_3$ 51.60% $\text{H}_2\text{O}$	3 { 0.18648 gm. $\text{NH}_4\text{CNS}$ 22.16% $\text{NH}_3$ (by wt.)
4 { 33.7% $\text{NH}_4\text{NO}_3$ 18.82% $\text{NH}_3$ 47.48% $\text{H}_2\text{O}$	5 { 12.9% $\text{CaCl}_2$ 22.9% $\text{NH}_3$ 64.2% $\text{H}_2\text{O}$	6 { 55.8% $\text{Ca}(\text{NO}_3)_2$ 25.77% $\text{NH}_3$ 18.43% $\text{H}_2\text{O}$
7 { 28.15% $\text{NH}_3$ 71.85% $\text{H}_2\text{O}$	8 { 64.88% $\text{NaI}$ 26.92% $\text{NH}_3$ 8.20% $\text{H}_2\text{O}$	

monia absorbed is somewhat smaller. A solution of calcium nitrate and ammonia seems to possess no special advantages over the lithium nitrate except that of cheapness. However, it does possess one disadvantage, that the presence of carbon dioxide, if by any chance this should get into the gases being scrubbed for removal of ammonia, would cause the

formation of a precipitate which remains in suspension. With continued use this might become objectionable and have to be eliminated from the solution.

Vapor-pressure measurements were made on a calcium chloride-ammonia solution containing 64% of water. While solid calcium chloride absorbs ammonia it does not liquefy, but an absorbent solution is formed with the addition of water. Curve 5 and Table V show the results obtained from measurements with this solution. This shows it to be an absorbent of the same general character as the calcium nitrate but the solution possesses the disadvantage of being corrosive to metals.

TABLE III (Curve 3).  
 $\text{NH}_4\text{CNS}:\text{NH}_3:\text{H}_2\text{O}$   
 $\text{NH}_3, 22.16\%$ ;  $\text{NH}_4\text{CNS},$   
 $0.18648 \text{ G. per cc.}$

Temp. °C.	Pressure mm.
-15.3	39.6
-8.03	62.0
-0.81	94.5
6.78	143.9
10.16	170.8
17.19	237.6
23.0	314.1
30.3	433.1
35.7	543.1

TABLE IV (Curve 4).  
 $\text{NH}_4\text{NO}_3:\text{NH}_3:\text{H}_2\text{O}$   
 $\text{NH}_3, 18.82\%$ ;  $\text{NH}_4\text{NO}_3,$   
 $33.7\%$ ;  $\text{H}_2\text{O}, 47.48\%$ .

Temp. °C.	Pressure mm.
-12.95	53.2
-7.25	73.5
0.10	109.0
7.98	159.5
10.95	188.0
18.80	272.5
27.72	405.0
35.20	555.7

Sodium iodide when treated with anhydrous ammonia gas changes to a creamy mass which on the addition of a little water forms a solution with a slight suspension, the character of which was not investigated but is probably due to impurity in the salt. Measurements were made on two solutions, one with 8.2% of water and the other with 51.6% of water. The results of these measurements are seen in Curves 2 and 8 and in Tables II and VII. The solution containing 8.2% of water crystallizes at  $-8^\circ$ .

TABLE V (Curve 5).  
 $\text{NH}_3:\text{CaCl}_2:\text{H}_2\text{O}$   
 $\text{NH}_3, 22.9\%$ ;  $\text{CaCl}_2, 12.9\%$ ;  
 $\text{H}_2\text{O}, 64.2\%$ .

Temp. °C.	Pressure mm.
-13.4	54.0
-5.01	88.6
1.8	129.8
2.45	136.5
9.27	193.1
16.42	272.6
23.06	370.1
29.75	498.2
35.60	640.3

TABLE VI (Curve 6).  
 $\text{NH}_3:\text{Ca}(\text{NO}_3)_2:\text{H}_2\text{O}$   
 $\text{NH}_3, 25.77\%$ ;  $\text{Ca}(\text{NO}_3)_2,$   
 $55.8\%$ ;  $\text{H}_2\text{O}, 18.43\%$ .

Temp. °C.	Pressure mm.
-12.1	82.6
-4.9	124.1
+3.97	202.3
11.0	291.1
18.0	413.0
25.0	575.3
32.4	782.7
....	....
....	....

TABLE VII (Curve 8).  
 $\text{NaI}:\text{NH}_3:\text{H}_2\text{O}$   
 $\text{NH}_3, 26.9\%$ ;  $\text{NaI}, 64.88\%$ ;  
 $\text{H}_2\text{O}, 8.2\%$ .

Temp. °C.	Pressure mm.
-14.6	87.52
-13.0	96.6
-9.6	120.3
-8.0	143.0
-0.9	190.3
6.0	276.0
13.07	394.8
20.07	551.8
26.9	753.8



Both ammonium nitrate and ammonium thiocyanate are substances that liquefy readily with anhydrous ammonia gas. Measurements made on two solutions of these salts are shown in Curves 3 and 4 and Tables III and IV. Curve 7 shows the vapor pressure of 28.15 % of ammonia in water simply for comparison.

### Action on Metals.

Qualitative tests showed that solutions of ammonium nitrate and ammonium thiocyanate in ammonia attacked iron and steel and their alloys with great rapidity. Calcium chloride-ammonia solution was found to be corrosive to a less extent. Solutions of calcium nitrate and sodium iodide did not show immediate action, so that quantitative measurements were made with these solutions.

The results after 3 months showed that no loss occurred from the action of calcium nitrate on machine steel and nickel steel, but ordinary iron was rather badly attacked. Almost identical results were obtained with sodium iodide solutions. While vapor-pressure measurements indicate the possibility of using these solutions for absorbing ammonia from the hydrogen and nitrogen mixture of gases used in ammonia synthesis, it must not be forgotten that the action of hydrogen on halogen compounds or on the thiocyanate might result in introducing into the gas small amounts of halogen or sulfur compounds that would be detrimental to the life of the catalyst. Therefore, of this set of solutions calcium nitrate seems most promising for use as an absorbent for the ammonia.

### Summary.

1. Vapor-pressure curves for solutions of several inorganic salts in ammonia have been constructed.

2. Solutions of ammonium nitrate in ammonia and ammonium thiocyanate are very corrosive to iron and steel; calcium chloride-ammonia is less corrosive, and calcium nitrate-ammonia and sodium iodide-ammonia show no immediate corrosive action.

3. Calcium nitrate-ammonia solutions seem the most promising of these solutions for practical use as an absorbent for ammonia in the synthetic process.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

## THE MAGNITUDES OF ATOMS.

BY THEODORE W. RICHARDS.

Received April 12, 1921.

Recently two interesting papers upon the diameters of atoms have been published, namely, those of W. L. Bragg<sup>1</sup> and A. Landé.<sup>2</sup> The former makes use of the method of X-ray reflection; whereas the latter depends upon Bohr's theory. In view of the fact that the results do not agree, it may be not uninteresting to point out that another much simpler and less recondite method of obtaining approximate estimates of diameters of some of the atoms in question under varying circumstances has been available for several years. This method, although it is probably no more uncertain than either of the methods mentioned above does not seem to have attracted general attention.

In a paper<sup>3</sup> summing conclusions concerning atomic volumes, I pointed out that from the study of the contractions which occur when elements combine together with the compressibilities of those elements, it is possible to draw a plausible inference as to the bulk which the elements occupy when combined. A graph (which had as its main object the proof that the magnitude of the contraction is dependent in part upon the magnitude of the compressibility of the factors) was given, depicting the compressibilities of the metals of the alkalis compared with the contraction occurring during the formation of their chlorides. This graph is represented in the uppermost curve of the accompanying diagram (Fig. 1) which now gives also corresponding curves for bromides and iodides.

"An interesting corollary suggested by this diagram is to be found in the extrapolation of the curve toward the left. The point where the abscissa becomes zero indicates the hypothetical contraction which would take place if an imaginary incompressible element were combined with chlorine by an affinity about equal to that of the others, to form a compound similar to lithium chloride." Since, in this case, the contraction of 12.5 cc. must be due to the 25.1 cc. of chlorine alone, we may suppose that in each of the actual cases of the alkali chlorides the contraction must be about the same, and that in each case the chlorine occupies about  $25.1 - 12.5 = 12.6$  cc. From this assumption and the actual total contractions, the hypothetical bulk which each atom must oc-

<sup>1</sup> W. L. Bragg, *Phil. Mag.*, [VI] 40, 169 (1920).

<sup>2</sup> A. Landé, *Z. Physik*, 1, 191 (1920); *C. A.*, 14, 2124 (1920). A discussion of allied questions took place recently in the Bunsen Gesellschaft, *Z. Physik*, 2, 309 (1921); *Z. Elektrochem.*, 26, 502 (1920).

<sup>3</sup> T. W. Richards, *THIS JOURNAL*, 36, 2417 (1914).

cupy in its chloride was computed. The numerical estimates are based, as has been said, upon the assumption that the chlorine is equally compressed by the several affinities of the alkali metals. The assumption is partially justified by the fact that the heats of formation of the sev-

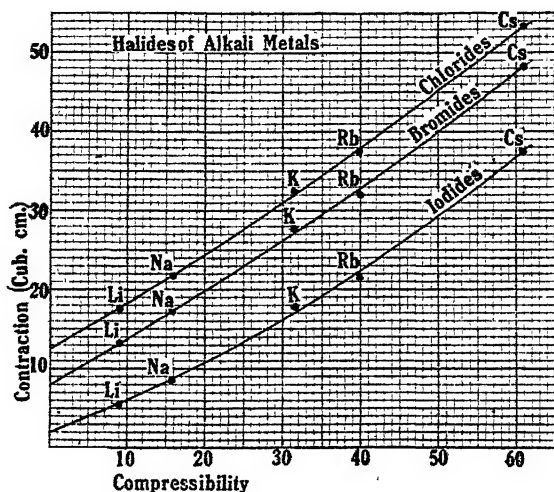


Fig. 1.

Fig. 1.—Graphs depicting the compressibilities of the alkali metals compared with the contraction during the formation of their halides. Contraction on combination in cc. per mol is plotted ordinately; compressibilities of the elements are plotted as abscissas.

eral chlorides are nearly the same, and by the further fact that in such cases heat of formation is not very different from free energy change. Because the possible error of a cubic centimeter or two would make very little difference in the atomic diameters, however, these values will nevertheless be adequate for the present purpose.<sup>4</sup> The probability is, that the affinity of the alkali metal increases somewhat as the atomic weight increases, which would make the volume of the chlorine somewhat less than 12.6 cc., especially in the cases of the heavier metals. Hence the values given below for the metals are minimal values.

<sup>4</sup>There is no need at present of attempting the analysis of the other questions which might affect such an estimate. In this latter category comes the question as to how nearly free energy change (which means the work which may be done in excess of that involved in the atomic compression) represents the force of affinity, and also the question as to the effect of the differing atomic volumes of the metals, which involve at the same time different bulks to be compressed and different surfaces exposed to pressure—circumstances partially counterbalancing one another. The heats of formation of the 5 alkali chlorides are respectively 392, 399, 431, 462, and 479 kilojoules.

On comparing the result for chlorides with those for bromides and iodides, it becomes evident that whereas the extrapolated value for the contraction of chlorides in forming alkali chlorides is about 12.6 cc., that of bromine on forming the alkali bromides is only about 8 cc. and that of iodine only about 2 cc. These latter figures (which likewise represent minimal values) are reasonable, since bromine in the elementary state is undoubtedly already much more compressed than chlorine. The so-called "atomic volumes" of bromine and iodine being respectively 25.6 and 25.7 cc., the bulks which these elements occupy in the bromides and iodides of the alkali metals can hardly exceed 17.6 and 23.7 cc. per gram atom respectively. Subtracting these values from the well-known molecular volumes of the halides we obtain the following values for the bulk of the metals in these compounds. As already said, all the figures for the metals being minimal values should probably be increased somewhat with increasing molecular weights; hence the table gives conservative evidence which can hardly fail to avoid exaggerating the differences to be emphasized.

TABLE I.—ATOMIC VOLUMES OF HALOGENS AND ALKALI METALS IN COMBINATION.  
(Cc. per gram Atom.<sup>a</sup>)

	In chlorides.	In bromides.	In iodides.
Halogen.....	12.60	17.60	23.70
Lithium.....	7.90	7.47	9.26
Sodium.....	14.45	14.53	17.21
Potassium.....	24.92	25.70	29.46
Rubidium.....	30.61	31.77	36.12
Cesium.....	29.74	30.39	33.90

\* The second decimal place is not significant with regard to the individual values, but is significant with regard to their sums, which are simply the "molecular volumes" of the salts. The densities (20°/4°) used in these calculations were as follows: for the 5 alkali metals, respectively, 0.534; 0.9712; 0.8621; 1.532; and 1.882; for the 3 halogens, respectively 1.412; 3.120; and 4.94; for the 5 chlorides respectively, 2.068; 2.161; 1.987; 2.798; and 3.974; for the 5 bromides respectively, 3.464; 3.203; 2.749; 3.349; and 4.433; for the 5 iodides respectively 4.061; 3.665; 3.123; 3.550; and 4.509. See T. W. Richards and F. N. Brink, *THIS JOURNAL*, 29, 117 (1907); G. P. Baxter, *Am. Chem. J.*, 31, 558 (1904); Baxter and Wallace, *THIS JOURNAL*, 38, 265 (1916). If Dewar's lower value for iodine were taken, the values for the bulk of the metals in the iodides would be somewhat reduced, but would still be much larger than the bulk in the bromides. (*Chem. News*, 91, 216 (1905)). The compressibilities recorded in Fig. 1 are those of Richards and Stull, *Carnegie Inst. Pub.*, 7 (1903), and 76 (1907).

This table is striking in its evidence (wholly consistent except in the case of lithium bromide), that the metals are in a less compressed state in the bromides than in the chlorides and in a still less compressed state in the iodides. Such an outcome is only reasonable, considering the undoubted difference in the affinities of the halogens for the alkali metals, and granting that affinity and cohesion produce pressure and are

thus capable of diminishing the volume of the atoms and molecules upon which they act.

That this method gives reasonable and consistent results is shown by a similar calculation involving the three halides of potassium. These, evolving respectively 431, 398 and 335 kilojoules in their formation show attendant volume changes of respectively —33.0, —27.7 and —18.0 cc. Extrapolating to zero compressibility both sets of values (plotted as above in relation to the compressibility of the halogen) to represent an imaginary incompressible halogen, we find that the heat of the formation of the imaginary halide of potassium would be 300 kj. and the attendant contraction (to be referred wholly to the potassium) about 14 cc. per mol. Assuming direct proportionality,<sup>5</sup> the 431 kj. evolved when potassium chloride is formed should then correspond to about 20 cc. contraction of the potassium. We have seen that the contraction of the chlorine is to be considered as about 12.6. The sum of these two values 32.6, is very near the actual contraction, 33.0. Hence we may reasonably believe that the contraction has been rightly apportioned between the two component elements, and therefore that the volumes of the combined atoms are known with rather surprising exactness.

The figures in the table just given record the so-called "atomic volumes" of the metals in the several halides. From these figures, thanks to the remarkable investigations of Millikan and Perrin and others, we are able to compute at once the bulks occupied by the individual atoms and therefore the diameters which they must possess. Assuming that each gram-atom contains  $6.062 \times 10^{23}$  atoms, the following table is obtained for the bulk of the individual atoms in question under the varying circumstances.

TABLE II.—VOLUMES OF INDIVIDUAL ATOMS UNDER VARYING CIRCUMSTANCES.

Each Value is Multiplied by One Septillion ( $10^{24}$ ) cc.

	In chlorides.	In bromides.	In iodides.
Halogen.....	20.8	29.0	39.1
Lithium.....	13.0	12.3	15.3
Sodium.....	24.3	24.4	28.4
Potassium.....	41.1	42.4	48.6
Rubidium.....	50.5	52.4	59.6
Cesium.....	49.0	50.1	55.9

Since in the halides, on account of the large volume changes and the intensity of compression, the atoms of the elements must be compressed

<sup>5</sup> The true relationship is doubtless not one of exact proportionality, but in the absence of knowledge as to its nature this may be assumed as a first approximation. Of course a similar correction should be applied to the halogens as given in the table, each of which must really have different values in combination with the different metals. Here, however, the affinities concerned being more nearly equal for any given halogen, this correction seemed to be a work of supererogation.

into nearly cubical form<sup>6</sup> (See Fig. 2), a close approximation to the distance between the faces of the atoms is to be obtained by simply tak-

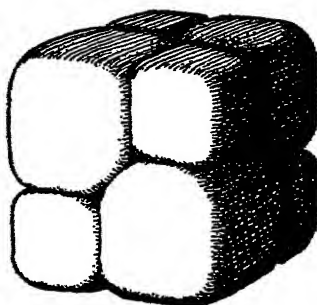


Fig. 2.

ing the cube roots of the volumes. This approximate distance in the case of chlorine is  $20.6 \times 10^{-24} = 2.75 \times 10^{-8}$  cm. The following table records the results.

TABLE III.—THE CUBE ROOTS OF THE VOLUMES OF INDIVIDUAL ATOMS UNDER VARYING CIRCUMSTANCES.

(Each Value expressed in Ångstrom units.)

	In chlorides.	In bromides.	In iodides.
Chlorine.....	2.75	....	....
Bromine.....	....	3.09	....
Iodine.....	....	....	3.39
Lithium.....	2.35	2.35	2.48
Sodium.....	2.90	2.90	3.05
Potassium.....	3.45	3.49	3.65
Rubidium.....	3.70	3.74	3.91
Cesium.....	3.66	3.69	3.82

A clearer insight into the meaning of these figures may be gained from a glance at the diagram, which, representing the arrangement in space of the atoms of the alkali halides, has since been essentially confirmed by W. H. and W. L. Bragg, and may be considered as fairly certain.<sup>7</sup> Incidentally attention may be called to the fact that the crystal must be built up of quadrimolecular units of this sort, not units with 3 atoms on each edge, since the latter unit (having 27 atoms in all) would have a surplus of one atom either of chlorine or metal.<sup>8</sup> Whether or not such cubes unite evenly so as to cause the crystal to be a single molecule does not greatly concern us at present.

<sup>6</sup> T. W. Richards, *THIS JOURNAL*, 35, 381 (1913); 36, 1686 (1914).

<sup>7</sup> Compare W. J. Sollas, *Proc. Roy. Soc.*, 63, 273 (1898), who first proposed this arrangement, without, however, postulating atomic compression. See also T. W. Richards, *THIS JOURNAL*, 35, 381 (1913).

<sup>8</sup> Compare W. H. and W. L. Bragg, "X-rays and Crystal Structure," 1916, p. 95.

A glance at the diagram shows that the data as given above in Table III need a slight correction, since they are computed for perfect cubes, and the "atomic domain" of the larger atom of her pita must have its cubic shape somewhat modified in order to attain perfect close packing. In other words, because of the basis of the calculation, it is necessary to account for *all* the molecular volume. This fact must cause the true distance between the atomic centers to be slightly greater than half the sum of any two of these cube roots—unless the two atomic volumes are identical, when half the sum of the roots gives the exact value. The true distance between the atomic centers may obviously be found by calculating the edge of the cube or crystal unit depicted in Fig. 2. Such a cube involves 4 molecules. The gram-molecular volume of CsCl is 42.34; hence of 4 CsCl, 169.36 cc. Dividing by  $6.062 \times 10^{23}$  and extracting the cube root of the result we have  $6.53 \times 10^{-8}$  cm., the exactly computed length of the edge of such a cube. The sum of the atomic diameters given in Table III is 6.40, a difference of 0.13 Ångstrom. This difference must be due to the modification of the larger of the two cubes at the inside edges, as shown in the diagram. Only in the cases of rubidium chloride and lithium iodide is any other deviation as great as this. Usually the effect is negligible.

Evidently, since the smaller cube of any pair is probably not essentially modified, its value may be taken as correctly given in the preceding table, and the distance between the faces of the larger atom may be computed as the difference between the total value and the smaller exact cube root from Table III. These distances may be called "atomic diameters" of which the corrected values are given in the table below, compared with the figures for the same elements obtained by Landé and Bragg respectively.

TABLE IV.—DIAMETERS ( $d$  OR  $d'$ ) OF INDIVIDUAL ATOMS OF ALKALI METALS AND HALOGENS (IN ÅNGSTROM UNITS).

	Landé.	Bragg.	T. W. R. In chlorides.	T. W. R. In bromides.	T. W. R. In iodides.
Chlorine.....	3.3	2.1	2.8	...	...
Bromine.....	3.6	2.4	...	3.1	...
Iodine.....	4.1	2.8	...	...	3.4
Lithium.....	...	3.0	2.3	2.4	2.6
Sodium.....	2.2	3.5	2.9	2.9	3.1
Potassium.....	2.9	4.2	3.5	3.5	3.7
Rubidium.....	...	4.5	3.8	3.8	3.9
Cesium.....	3.2	4.7	3.8	3.7	3.8

It is striking that the newly recorded values all lie about half way between those of Landé and those of Bragg. Landé's results for the halogens are all much larger, and accordingly, his results for the metals all much smaller than the other estimates. One cannot help thinking that

Landé's estimates are in error, especially because his value for iodine, for example, corresponds with an "atomic volume" of this element in iodides of 38.8 cc., which means an *expansion* per 127 g. of iodine of over 13 cc. in the act of forming an iodide. All evidence upon the question of volume change in chemical reaction contradicts such a conclusion. Nevertheless it is interesting that Landé's figures, depending upon hypothetical assumptions, should be as close to the others as they are.

Bragg's results, depending much more closely upon experiment, are safer, but seem to demand a rather excessive contraction of halogen. For example, a gram-atom of chlorine in the act of combination, is made to contract from 25.1 cc. to 5.6 cc., which seems unlikely. Probably the method of calculation (which involved no consideration of the changing volume of an atom under varying affinity-pressures) must have caused this anomaly. While admitting that the atom (or its "sphere of influence") might change somewhat in size, he does not appear to have correlated different values in relation to the affinities concerned.

Bragg's statement<sup>9</sup> that the cesium atom, when combined with a halogen, occupies less space than the rubidium atom, is verified by these new results. He points out that with oxygen compounds of cesium the reverse is the case. May not the reason for this apparent contradiction be simply that the affinity of cesium for the halogens is much greater than the affinity of cesium for oxygen? The heat of oxidation of a gram-atom of cesium is only 172 kj., whereas  $\text{Cs} + \text{Cl}$  evolves 479 kj. In the case of a very compressible element like cesium this difference of affinity is quite enough to account for the apparent contradiction, and all the results fall thus into line.

The importance of change of volume under the influence of chemical affinity and cohesion, in any such calculations, cannot be over-estimated. The arguments in favor of it, based upon the comparative volumes of liquids and solids, are so convincing as to leave no doubt concerning the magnitude of the changes involved.<sup>10</sup> They are not matters of theory, but the actual result of the comparison of accurately determined molecular volumes of elements and compounds. For example, 70.6 cc. of cesium combines with 25.1 cc. of liquid chlorine (95.7 cc. in all) to make only 42.34 cc. of cesium chloride. That such contractions are greater the greater the compressibilities of the elements concerned, is likewise clear, and so is the effect of the cohesion of the product.

The fact that the "atomic domain," or "sphere of influence," or "atomic playroom," or "practical bulk of the atom," (as this space has been variously called) thus changes, makes the assignment of any fixed volume to it under varying conditions illusory. The only reason why definite

<sup>9</sup> W. L. Bragg, *Phil. Mag.*, [6] 40, 174 (1920).

<sup>10</sup> T. W. Richards, *THIS JOURNAL*, 36, 2417 (1914).



bulks could be assigned as a first approximation to chlorine, bromine and iodine in the last three columns of Table III, is because the affinities of any one of these halogens for the different alkali metals are so nearly alike that the extent of chemical and cohesive compression of any one halogen must be nearly the same when in combination with each of the five metals. But even here this assumption cannot be absolutely correct although it serves as the basis of a conservative first approximation. Correction for this error would bring new results somewhat nearer to Bragg's, but apparently could not, in any probability, give volumes of the metallic atoms as large as he makes them.<sup>11</sup>

There is nothing, in the present paper, inconsistent with the brilliant experimental results of the Professors Bragg. The only premise needed for the construction of a completely consistent scheme from all these varied data seems to be the recognition of the almost certainly ascertained conclusion that affinity and cohesion are capable of altering the "atomic domain," and that the compressibilities of the factors affect the outcome. Taking all these considerations together it is evident that there has been attained an insight into the actual magnitudes of the space demanded by atoms in crystals which was not dreamed possible twenty years ago.

The bearing of these conclusions upon the "valency volume" hypothesis of Pope and Barlow may be noted, but needs no discussion.<sup>12</sup>

### Summary.

In brief it is pointed out that the contraction suffered during combination, taken in connection with the compressibilities of the elements combined, makes possible an approximate estimate of the bulk occupied by the several constituents in a compound.

Calculations are made for the diameters of the atoms of the halogen and the alkali metals, which diameters are found to lie about half-way between the results of Bragg and those of Landé.

Emphasis is placed upon the importance of considering the compressing effect of the affinities concerned, in making any comparison of atomic volume.

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<sup>11</sup> In a careful calculation (too complicated to be worth printing in this brief notice) in which maximum allowance was made for all reasonable corrections to these results, only one of them (CsI) was changed more than 0.1 Ångström. In this one case the "atomic volume" of the combined iodine found was only 19 cc. instead of 23.7, which makes the atomic diameter of this element 3.15 instead of 3.39 Ångström. This corrected value would make the diameter of the Cs atom 4.09 instead of 3.85. Most of the values given above were practically unchanged by this calculation.

<sup>12</sup> W. J. Pope and W. Barlow, *J. Chem. Soc.*, 89, 1675 (1906); T. W. Richards, *THIS JOURNAL*, 35, 381 (1913); 36, 1686 (1914); W. J. Pope and W. Barlow, *ibid.*, 36, 1575, 1695 (1914).

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.<sup>1</sup>]

## THE ENTROPY OF ELECTRON GAS.

BY RICHARD C. TOLMAN.

Received April 21, 1921.

## 1. Introduction.

It has become increasingly evident that physical chemists can achieve considerable simplification in mode of expression and thought by treating electrons as the atoms of a chemical substance. Just as we speak of the substance chloride ion and write for it the formula  $\text{Cl}^-$ , we may speak of the substance electron and write for it the formula  $\text{E}^-$ , and the use of such symbols in electrochemistry has already become usual.

In the case of the electrons given off from a heated filament we may properly speak of the substance electron gas. Richardson<sup>2</sup> and his co-workers have indeed shown that these electrons are actually emitted with velocities which are distributed in the different directions in accordance with Maxwell's distribution law for the molecules of a gas which cross any plane boundary. Whatever the distribution of emitting velocities may be, however, if we had an evacuated vessel with walls made from the filament substance and raised the walls to a high temperature, the vessel would fill with electron gas which would exert a definite vapor pressure, depending on the temperature of the walls. Laue<sup>3</sup> has recently made an elaborate investigation of the conditions under which this gas will obey the perfect gas laws, while the application of thermodynamic reasoning to the behavior of the gas has been made familiar by the work of H. A. Wilson,<sup>4</sup> Richardson<sup>2</sup> and others.

Owing to the very considerable force of repulsion between electrons, the conditions under which this gas will not deviate appreciably in behavior from a perfect monatomic gas are more stringent than for most monatomic substances, which usually have a moderate attraction between molecules rather than a strong repulsion. In order for electron gas to obey the perfect gas laws, the concentration must be low enough and the temperature high enough so that the effects produced by the repulsive force between the electrons can be neglected in comparison with effects produced by their thermal agitation. Furthermore, on account of the mutual repulsion of the electrons, the dimensions of the containing vessel must be small unless we are willing to allow a higher concentration at the periphery than in the center of the gas. And finally the containing walls

<sup>1</sup> Published by permission of the Chief of Ordnance.

<sup>2</sup> Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green and Co., London, 1916.

<sup>3</sup> Laue, *Ann. Physik.*, **58**, 695 (1919).

<sup>4</sup> H. A. Wilson, *Phil. Trans.*, **202A**, 258 (1903).

must all be of the same material and at the same temperature since otherwise the Volta effect will set up differences in electric potential between different portions of the vessel which will destroy the uniform concentration of the gas.

It should be noted that these restrictions which are necessary in order that the perfect gas laws may apply are of the same nature and merely more stringent than those encountered in the case of more familiar gases. All gases obey the perfect gas laws more closely as their concentration is made lower and their temperature higher. Furthermore in large masses of gas the gravitational attraction of the gas for itself leads to an increased concentration at the center analogous to the increased concentration at the periphery in the case of electron gas. Finally the local disturbances in concentration which would be produced by differences in potential between different parts of the containing walls are entirely analogous to the differences in concentration which may be produced in ordinary gases by the gravitational effect of external bodies.

Perhaps the most distinguishing characteristic of electron gas is that it is apparently a gas which is *plus que parfait* at all temperatures and pressures while most gases are *moins que parfait* throughout the greater range of temperature and pressure. It should also be pointed out that the mechanism by which electron gas exerts its pressure is obviously not that of the older kinetic theories which assumed a bombardment of the walls by rigid elastic molecules. This consideration, however, need cause us no concern, since we have already learned even in the case of more familiar gases to regard the above mechanism at least as no better than a first approximation. In the case of any gas dilute enough the exact nature of the mechanism by which the momentum is transferred to the walls has no effect on the final value of the pressure.

## II. Theoretical Equation for the Entropy of Electron Gas.

Assuming now that we have electron gas under such conditions that it obeys the laws for a perfect monatomic gas law we may evidently write for its entropy per mol,

$$S = 5/2 R \ln T - R \ln p + \text{const.} \quad (1)$$

With regard to the constant occurring in Equation 1, Laue<sup>5</sup> has already made the suggestion that this constant will depend on molecular weight in the same way as has been found for other monatomic gases. If this be true, we may rewrite Equation 1 in the form

$$S = 5/2 R \ln T - R \ln p + 3/2 R \ln M + S_1 \quad (2)$$

where  $M$  is the molecular weight of the electron and  $S_1$  has the same value for all monatomic gases

<sup>5</sup> Laue, *Jahr. Radioakt. Elektronik*, 15, 257 (1918).

In a recent article<sup>6</sup> the author has shown the possibility of deriving Equation 2 in a very simple way from the principle of similitude or relativity of size, and has found that the entropy of a number of monatomic gases at 25° is closely given by Equation 2 when  $S_1$  is given the value 24.27,<sup>7</sup>  $S$  and  $R$  being in calories per degree,  $T$  in degrees centigrade absolute,  $p$  in dynes per sq. cm. and  $M$  the molecular weight in grams.

The main purpose of the present article is to show that the entropy of electron gas as calculated from Equation 2 actually agrees with the entropy of the electron gas in equilibrium with tungsten, tantalum and molybdenum filaments at 2000° absolute as calculated from the heat known to be absorbed when electrons are emitted from the hot filaments. Having thus assured ourselves of the probable validity of Equation 2, we shall then make use of this equation in a following article to study the thermal ionization of gaseous vapors at high temperatures.

**Pressure of Electron Gas in Equilibrium with Hot Filaments.**—In order to apply Equation 2 to the electron gas in equilibrium with hot filaments, we must evidently have a value for the pressure of the gas in equilibrium with the filament. Now there is a well-known relation between the pressure of a gas  $p$ , and the number of mols of gas  $N$  which cross a plane surface of unit area in unit time. This relation may be written in the form,

$$N = \frac{p}{\sqrt{2\pi M R T}} \quad (3)$$

and can be simply derived merely from the assumption that the velocities of the molecules are distributed in accordance with Maxwell's distribution law.

In the case of a filament in equilibrium with an electron gas, Equation 3 will determine the number of electrons impinging on unit area of the filament in unit time. Since we have equilibrium the number impinging

<sup>6</sup> Tolman, *THIS JOURNAL*, 42, 1185 (1920).

<sup>7</sup> In the article referred to, it was shown that the entropy of a number of monatomic gases at 298° K and one atmosphere pressure could be calculated from the formula,

$$S = \frac{3}{2} R \ln M + 25.1 \text{ calories per degree per mol.}$$

Comparing with Equation 2, it is evident that we may write,

$$\frac{5}{2} R \ln T - R \ln p + S_1 = 25.1$$

Putting  $R = 1.985$  calories per degree,  $T = 298^\circ \text{K}$ ,  $p = 1,013,200$  dynes per sq. cm., and solving for  $S_1$  we obtain the value 24.27.

Some of the methods for deriving Equation 2 based on the quantum theory lead to a theoretical value for  $S_1$ . Nevertheless a complete agreement as to this theoretical value does not yet seem to have been achieved. For this reason it has seemed to the present writer desirable to use the experimental value.

on the filament surface must be equal to the number leaving the surface, and this latter will be equal to the number reflected by the surface plus the number freshly emitted by the surface. If  $r$  is the fraction of the impinging electrons which are reflected and  $i$  is the saturation current per unit area which can be obtained when all the electrons emitted by the surface are removed as fast as formed, and we assume that the emission of electrons from the hot filament takes place in the same way under equilibrium conditions as when the saturation current is being measured, we may write as an expression for the equality of the number of electrons impinging on the surface and leaving the surface per unit time,

$$N = r N + \frac{i}{F} \quad (4)$$

where  $F$  is the Faraday (*i. e.*, the quantity of electric charge carried by one mol of electrons). Substituting the value of  $N$  given by Equation 3 and solving for the pressure  $p$ , we obtain,

$$p = \frac{i \sqrt{2 \pi M R T}}{F (1-r)} \quad (5)$$

In order to use this equation for the case of the electrons in equilibrium with hot filaments we shall use Langmuir's<sup>8</sup> careful measurements of the saturation currents for tungsten, tantalum and molybdenum filaments at 2000° K, as given in the second column of Table I. For  $M$ , the molecular weight of the electron we shall take  $5.44 \times 10^{-4}$  g., for  $R$ ,  $8.315 \times 10^{-7}$  ergs per degree per mol, for  $T$ , 2000° K, and for  $F$ , 96540 coulombs.

As to the value for  $r$  for the fraction of the electrons reflected we have very meager data. Richardson<sup>9</sup> estimates that about 30% of the slow moving electrons present in the absence of an electric field are reflected from a brass surface. Gehrts<sup>10</sup> found 42% reflection for aluminum, 58% for lead, 52% for cobalt, 56% for copper and 10% for lamp-black surfaces with electrons which had been emitted from a copper plate by the action of ultra-violet light and then accelerated by a drop of potential of 2 volts. When no voltage drop was applied the percentage reflection was less in those cases where measurements were actually made, but there is some uncertainty as to the exact interpretation of the results owing to the possible disturbing effect of gas molecules left in the evacuated tube.

Fortunately very exact information as to  $r$  is not necessary, since it will be seen from an examination of Equations 2 and 5 that it enters into the final expression for entropy as an additive term of the form,

$$R \ln(1-r).$$

<sup>8</sup> Langmuir, *Trans. Electrochem. Soc.*, 29, 125 (1916).

<sup>9</sup> Richardson, *loc. cit.*, p. 155.

<sup>10</sup> Gehrts, *Ann. Physik.*, 36, 995 (1911).

If  $r$  has the value zero this term has the value zero. If  $r$  should have a value as great as 0.5, the whole term would only have the value of 1.4 entropy units in a total which is going to be about 50 entropy units. Under the circumstances we shall neglect the reflection altogether and put  $r = 0$ .

Substituting the above numerical values into Equation 5 we have obtained values for the pressures of the electron gas in equilibrium with the filaments, as given in the third column of Table I. It will be seen that the pressures of the electron gases in equilibrium with these filaments are so exceedingly low as to give us confidence in our assumption that the gas laws are valid.

TABLE I.

Filament.	$i_{2000^\circ}$ .	$\frac{\text{amperes}}{\text{sq. cm.}}$	$p \frac{\text{dynes}}{\text{sq. cm.}}$	$S_{2000^\circ}$ .
Tungsten.....	0.0042		$1.037 \times 10^{-8}$	53.3
Tantalum.....	0.007		$1.729 \times 10^{-8}$	52.3
Molybdenum.....	0.013		$3.210 \times 10^{-8}$	51.0

**Numerical Values of Entropy from Equation 2.**—We are now ready to substitute into the theoretical Equation 2. Expressing entropy in calories per degree we shall take  $R = 1.985$  calories per degree,  $T = 2000^\circ \text{ K}$ ,  $M = 5.44 \times 10^{-4}$  grams, and  $S_1 = 24.27$ . Substituting these values together with the pressures just determined into Equation 2 we have obtained the values for the entropy of the electron gases given in the fourth column of Table I.

### III. Calculation of the Entropy of Electron Gases from Heat of Vaporization.

It has long been realized from the work of Richardson, that the emission of electrons from a hot filament is accompanied by an absorption of heat. This was made evident in the first place by the great temperature coefficient for the thermal emission of electrons. More recently, however, Richardson<sup>2</sup> has actually shown and measured the cooling of a filament when a given number of electrons are allowed to escape and the inverse effect of heating when the electrons are absorbed. Fairly exact measurements of the cooling effect have more recently been made by Lester.<sup>11</sup>

If  $\Delta H$  is the heat absorbed when a mol of electrons is reversibly evaporated at temperature  $T$ , it is evident that the increase in entropy of the system will be given by the equation,

$$\Delta S = \frac{\Delta H}{T}. \quad (6)$$

<sup>11</sup> Lester, *Phil. Mag.*, 31, 197 (1916).

This increase in entropy is obviously equal to the entropy  $S$  of the electron gas which has been formed plus the change in the entropy of the metal  $\Delta S_m$  which occurs when one mol of electrons is removed, so that we may rewrite Equation 6 in the form,

$$S = \frac{\Delta H}{T} - \Delta S_m. \quad (7)$$

The quantity  $\Delta S_m$  which is the change in the entropy of a large quantity of metal when one mol of electrons is removed is presumably small, since owing to the small mass of electrons and the strong constraints under which they are held within the metal they are known from specific heat data to pick up thermal energy only very slowly as the temperature is raised above the absolute zero. For example, in the case of tungsten, the specific heat at room temperature ( $300^\circ \text{K}$ ) is known to have about the theoretical value  $C_v = 6.0$ , predicted on the assumption that the electrons have acquired no thermal energy. At  $2000^\circ \text{K}$  Worthing<sup>12</sup> finds  $C_v = 7.0$ . If we assumed that the partial specific heat of the electrons over the whole range from  $300^\circ \text{K}$  to  $2000^\circ \text{K}$  were the whole difference between these figures or one calorie per degree, the partial entropy acquired by all the electrons in one mol of tungsten at  $2000^\circ$  would only be 1.9 entropy units. Under the circumstances we shall feel justified in neglecting the change in the entropy of the metals in question when the electrons are evaporated and shall write directly,

$$S = \frac{\Delta H}{T} \quad (8)$$

where  $S$  is the entropy of the electron gas, the same quantity which we have already calculated from the theoretical Equation 2.

**The Heat of Vaporization of Electron Gas.**—In order to carry out the calculations indicated by Equation 8, we shall make use of the direct determinations of Lester<sup>11</sup> of the heat lost by a filament when electrons are evaporated from it. These measurements were made by comparing the change in the resistance of a filament produced by the cooling effect of electron emission with the change in resistance produced by a known change in the current used for heating the filament.

Lester has calculated his results on the assumption that the electrons leaving the hot filament have the kinetic energy  $2RT$  per mol which, in accordance with Maxwell's distribution law is the average kinetic energy of the molecules of a gas which cross any plane boundary in a given time interval. Since the experimental results of Richardson<sup>13</sup> and his co-workers have actually demonstrated that the velocities of the electrons emitted from a hot filament are distributed in accordance with the Max-

<sup>12</sup> Worthing, *Phys. Rev.*, 12, 199 (1918).

<sup>13</sup> Richardson, *op. cit.*, p. 139 and following.

well law, we may accept this assumption. Lester's calculations also assume that the electrons in the metallic part of the circuit bring with them into the hot filament the energy  $2RT_c$  where  $T_c$  is the temperature of the cool part of the circuit. This latter assumption is presumably not an exact approximation of the truth. Nevertheless the whole correction term,  $2R(T - T_c)$ , is only a few per cent. of the total heat effect so that our lack of exact information is not serious.

Lester's results may be expressed with the help of the equation,

$$P = F\phi + 2R(T - T_c) \quad (9)$$

where  $P$  is the actual energy input per second which Lester found was necessary in order to produce the same numerical change in filament temperature as was produced by the evaporation of one mol of electrons per second;  $F$  is the Faraday or quantity of electricity carried by one mol of electrons,  $\phi$  is the equivalent potential drop which the electrons have to overcome in escaping through the surface of the metal and the correction term  $2R(T - T_c)$  has the significance already discussed.

For  $\phi$  Lester gives the values in volts shown in the second column of Table II. If we multiply  $\phi$  by  $F = 96540$  coulombs, we find the energy input in joules necessary to take one mol of electrons across the boundary of the metal, under the conditions of the experiment and shall assume this same energy input necessary for a reversible evaporation. In order to get the reversible heat of vaporization we must add to the energy input the quantity  $RT$  which is the external work that would have to be done against a movable piston if one mol of electrons were reversibly evaporated. We obtain for the heat of vaporization,<sup>14</sup>

Taking  $T = 2000^\circ \text{K}$  and expressing  $\Delta H$  in calories, the values obtained are given in the third column of Table II. Substituting in Equation 8

<sup>14</sup> It should be noted that this expression for  $\Delta H$  is based on Lester's assumption that the electrons in a metal at temperature  $T$  have the same mean kinetic energy as the molecules of a perfect gas at the same temperature, which does not agree with the low specific heat of metals already referred to above in connection with our estimate of  $\Delta S_m$ .

If we assumed that the electrons in the metal had no kinetic energy, we could then get  $\Delta H$  as follows. Take Lester's value of  $P$ , subtract  $2RT$  which is the kinetic energy of the escaping electrons when the saturation current is being measured, add  $\frac{3}{2}RT$  which would be the kinetic energy of the electrons in the space surrounding the filament of electrons under equilibrium conditions and add  $RT$  for the external work. We should obtain

$$\Delta H = P - 2RT + \frac{3}{2}RT + RT$$

or substituting Lester's expression for  $P$

$$\Delta H = F\phi + \frac{3}{2}RT - 2RT_c$$

Since  $T_c$  was actually a little less than  $T$ , it will be seen that expression used above for  $\Delta H$  was not greatly different from that which would be calculated by this other method.

$$\Delta H = F\phi + RT.$$



we obtain the values given in the fourth column of Table II for the entropy of one mol of electron gas in equilibrium with tungsten, tantalum and molybdenum filaments at 2000° K. For comparison the values calculated by the theoretical Equation 2 are given in the last column of the table.

TABLE II.

Filament.	$\Phi$ volts.	$\Delta H$ .	$S = \frac{\Delta H}{T}$ .	$S$ by Equation 2.
Tungsten.....	4.478	107270	53.6	53.3
Tantalum.....	4.511	107970	54.0	52.3
Molybdenum.....	4.588	109770	54.9	51.0

#### IV. Discussion.

**The Data Selected.**—The three filaments considered, namely, tungsten, tantalum and molybdenum are the only ones for which both Langmuir has given values of the saturation current and Lester values of the heat of vaporization. Values for the heat of vaporization  $\Delta H$  might also have been obtained by making use of the Clausius vapor-pressure equation,

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$$

by substituting the value for pressure  $p$  in terms of saturation current  $i$  given by Equation 5,

$$p = \frac{i \sqrt{2\pi M RT}}{F(1-r)}$$

This would permit us to extend our considerations to any filament for which we have accurate values of the saturation current and the rate of change of saturation current with the temperatures. The comparisons seemed more conclusive, however, if we restricted ourselves to the case, of heats of vaporization which have been directly determined. Moreover it should be noted that in using the indirect method of determining heats of vaporization, we should have to introduce the additional assumption that  $dr/dT$  as well as  $r$  is a negligible quantity. Furthermore, the data on the rate of change of saturation current with temperature are usually expressed with the help of Richardson's original formula  $i = aT^{3/2} e^{b/T}$  where  $a$  and  $b$  are constants, and since this formula has no completely satisfactory theoretical justification, we might be led into error if we made use of it over a wider range of temperature than that in which it is empirically reasonably valid.<sup>15</sup>

<sup>15</sup> Making use of Langmuir's data (*loc. cit.*,) for the rate of change of saturation current with the temperature, and calculating  $\frac{\Delta H}{T}$  by the method described above, the

following results have been obtained for the entropy of electron gas in equilibrium with

**The Agreement.**—The agreement between the values for the entropy of electron gas as given by the theoretical Equation 2 and as calculated from the known heats of vaporization agree very well as shown in the last two columns of Table II. It is believed that the results may be taken as an adequate proof that the entropy of a dilute electron gas may be calculated from the same theoretical equation as has been found to apply to other monatomic gases. Of course, an exact agreement between the two methods of calculation is hardly to be expected, first because of experimental error in the data employed and secondly because of a number of assumptions which had to be introduced in the course of the calculations in order to arrive at any conclusions at all.

**The Assumptions.**—A recapitulation and discussion of these assumptions will not be out of place.

(a) In order to obtain Equation 5 for the relation between saturation current and the pressure of the electron gas in equilibrium with a hot filament, it was assumed that the same number of electrons will be given off per second by a hot filament, when electron gas is in equilibrium with the filament and when the saturation current is being determined. A partial justification for this assumption is provided by the fact that the current is found to be independent of the anode potential as soon as a high enough voltage drop has been applied to overcome the backing up effect of the space charge. With the Coolidge X-ray tube this has been shown to be true even at voltages above 100,000 volts.<sup>16</sup> Under the circumstances, we may conclude that the electron emission will not be decreased by the small-potential drop in the opposite direction present under equilibrium conditions.

To complete the justification for our assumption that the electron emission is the same under equilibrium conditions when the saturation current is being determined, we also need assurance that under equilibrium conditions no secondary emission is produced by electrons which bombard the emitting walls, since such a bombardment is not present when the saturation current is being determined. This seems to be justified in view of the work of Gehrts, already referred to, which shows that a potential drop of about 11 volts is necessary to produce secondary emission in the case of surfaces of aluminum, lead, cobalt and copper, and this for hot filaments at 2000° K. The values given in the last column are those obtained from the theoretical Equation 2 by the method already described.

Filament.	$S = \frac{\Delta H}{T}$ .	$S$ theoretical.
Tungsten .....	54.1	53.3
Tantalum .....	51.6	52.3
Molybdenum .....	51.6	51.0
Thorium .....	40.7	31.1

<sup>16</sup> Coolidge, *Phys. Rev.*, 2, 409 (1913).

sponds to a much higher kinetic energy than that of the average molecule at 2000°.

(b) In making actual calculations of the pressure with the help of Equation 5 it was assumed that the reflecting power of the hot metals in question is zero. This is probably not strictly true, in view of the work of Gehrts<sup>10</sup> on the reflecting power of a number of cold metallic surfaces. Nevertheless the effect of possible condensed layers of gas might increase the reflecting power of cold surfaces such as those with which he worked. Moreover, as already pointed out, a reflecting power anywhere between 0 and 50% would have but little effect on the final value of the entropy.

(c) In calculating the entropy of electron gas from its heat of vaporization, we have assumed that the values of Lester for the heat of vaporization when the vaporized electrons are being removed as fast as emitted is the same as the heat of vaporization under equilibrium conditions. This assumption is obviously closely connected with assumption (a) that the emission of electrons takes place to the same extent under equilibrium conditions and when the saturation current is being determined. Since assumption (a) occurred in the first method of calculating entropy and assumption (c) in the second method of calculation, the errors introduced, if any, may have cancelled out.

(d) In calculating the entropy of electron gas from its heat of vaporization, we have also neglected the change in the entropy of a metal produced by a change in its electric charge. This assumption is probably not strictly correct. The electrons in a metal, however, are held by strong constraints and have a small mass and hence pick up appreciable amounts of thermal energy only at high temperatures where, in accordance with the fundamental equation  $dS = dQ/T$  the rate of increase in entropy compared with the rate of increase in heat content is small.

**Conclusion.**—It is believed that this article establishes with reasonable certainty the possibility of calculating the entropy of electron gas from the theoretical equation which has been found to apply to other monatomic gases, namely,

$$S = \frac{5}{2} R \ln T - R \ln p + \frac{5}{2} R \ln M + S_1$$

where  $S_1$  has the same value for all monatomic gases.

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## LANGMUIR'S THEORY OF THE ARRANGEMENT OF ELECTRONS IN ATOMS AND MOLECULES.

BY CHARLES R. BURY.

Received April 28, 1921.

Langmuir<sup>1</sup> pictures an atom as consisting of a positively charged nucleus and electrons, equal in number to the units of positive electricity with which the nucleus is charged (or the atomic number of the element), which are arranged in concentric spherical shells of equal thickness round the nucleus. The electrons, though free to rotate or oscillate about their mean positions, are definitely localized in the atom. They are situated in cells, all of equal volume in any given atom: since there are 2 cells in the inner shell, there will be 8 in the second, 18 in the third and 32 in the fourth.

In his fourth postulate, Langmuir states that each cell can contain two electrons, except the two cells in the inner shell, which can contain only one: and that there can be no electrons in the outer shell until all the inner shells contain their maximum numbers of electrons.

By substituting an alternative to this fourth postulate it is possible to get a series of atomic structures similar to those obtained by Langmuir for the elements of lower atomic weight than sodium, but different for those of higher atomic weight. These structures are preferred by the author for the following reasons: (1) they give a better explanation of the chemical properties of the elements; (2) the necessity of postulating cells "independent of the electrons in them" is avoided. At the same time, the inconsistency that some cells can contain two electrons, others only one, is also avoided. The alternative postulate is as follows. The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus, successive layers can contain 2, 8, 18 and 32 electrons. Groups of 8 and 18 electrons in a layer are stable, even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8: more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure.

**The Two Short Periods.**—This postulate will leave unaltered the structures assigned by Langmuir to the elements of the first short period.

Sodium will have 2 electrons in the inner layer, 8 in the second, and one in the third; an arrangement that can conveniently be abbreviated as

<sup>1</sup> Langmuir, *THIS JOURNAL*, 41, 868 (1919).

(2,8,1). The succeeding elements in the second short period will each have one more electron in the third layer, up to argon with the structure (2,8,8), its chemical properties being attributed to the stability of the group of 8, not to the outer layer being complete, for the third layer can contain 18 electrons. For the structure of the elements of this period, Langmuir doubles the electrons in the cells of the second layer. The proposed alteration of structure suggests no difference in chemical properties from those deduced by Langmuir.

**The First Long period.**—Since 8 is the maximum number of electrons in the outer layer, potassium, calcium and scandium must form a fourth layer, although their third is not complete. Their structures will be (2,8,8,1), (2,8,8,2) and (2,8,8,3).

The elements from titanium to copper form a transition series, in which the stable but incomplete group of 8 in the third layer is changed to a saturated group of 18. With the accumulation of 4 electrons in the fourth layer of titanium, there is the possibility of some of them passing into the third unsaturated layer. These transition elements can have more than one structure, and the following are possible structures that the elements assume in their various compounds.

Ti	(2,8,8,4)	(2,8,9,3)	(2,8,10,2)		
V	(2,8,8,5)	(2,8,9,4)	(2,8,10,3)	(2,8,11,2)	
Cr	(2,8,8,6)	(2,8,11,3)	(2,8,12,2)		
Mn	(2,8,8,7)	(2,8,9,6)	(2,8,11,4)	(2,8,12,3)	(2,8,13,2)
Fe	(2,8,10,6)	(2,8,12,4)	(2,8,13,3)	(2,8,14,2)	
Co	(2,8,13,4)	(2,8,14,3)	(2,8,15,2)		
Ni	(2,8,14,4)	(2,8,15,3)	(2,8,16,2)		
Cu	(2,8,17,2)	(2,8,18,1)			

Of course, many more possibilities might be predicted. The question why only stable compounds corresponding with some of the possibilities exist and why unstable compounds correspond with others, while some possibilities are not represented in any known compounds, can be only partly answered. An accumulation of 4 electrons in the outer layer suffices in favorable circumstances to send one of them into the inner layer, but the tendency for one out of a group of 3 electrons to pass into the inner layer will be much less, while the tendency for 2 electrons to force one of themselves into the inner layer will be very small. This accounts for the great instability of the divalent salts of titanium, vanadium and chromium, in which they will have the structures (2,8,10,2), (2,8,11,2) and (2,8,12,2). Only one element, copper, forms a series of monovalent salts, in which it will have the structure (2,8,18,1), this structure being made possible by the stable group of 18 in the third layer. On the other hand, once several electrons have been forced into the third layer, the group of 8 is destroyed, and further electrons do not meet with the same resistance in passing into the third layer. Finally, in cobalt, nickel

and copper, the stable group of 8 in the third layer is impossible: such a structure would involve more than 8 electrons in the fourth, or the formation of a fifth layer. Electrons meet with little resistance in passing into the inner layer: the elements have no tendency to form compounds in which they exhibit a high valence, and their divalent salts are found to be the most stable.

The octet theory of valence in its plain straightforward form applies to the compounds of these elements: and this method of treatment compares favorably for practical convenience and simplicity with the elaborate arrangement of electrons in molecules which Langmuir's structures demand for the elements, while at the same time it affords a satisfactory explanation of their chemical properties. Thus manganese, in the permanganates, has the structure (2,8,8,7), and differs from chlorine (2,8,7), in its kernel only, just as chlorine differs from bromine, but not in the outer layer of electrons, on which the valence and type of compound depend. In chromates, manganates and ferrates, the metals have the structure (2,8,8,6), (2,8,9,6) and (2,8,10,6), having the same outer layer as sulfur (2,8,6) or selenium (2,8,18,6), but their kernels resemble each other far more than they resemble the kernels of sulfur or selenium; consequently, while they resemble sulfates and selenates, they resemble each other more closely. If Langmuir's structures for these elements are accepted, they should show no more resemblance than such series as carbon dioxide, nitrogen peroxide and ozone, or silica, phosphorus tetroxide, sulfur dioxide and chlorine peroxide. In the manganites, ferrites and in the dioxides of manganese, iron, cobalt, and nickel, the metals have 4 electrons in their outer layers. In their trivalent salts which all the transition elements except copper form, they have three electrons in their outer layers; and in their divalent salts, which they all form, they have only two. Throughout this transition series of elements, similar compounds are attributed to the elements having a similar outer layer of electrons, and differing only in their kernels.

It seems impossible to give a rational explanation of the chemical properties of such an element as manganese unless the possibility of more than one structure is postulated. Langmuir is driven to inconsistency in attempting to ascribe a structure to sodium manganate. Its chemical properties demand that the manganese atom should form an octet, but there is one electron too many. According to Langmuir's postulates there is no room for it in the inner layers; he has to invent a fresh position for electrons in the atom; the extra electron is held prisoner between the kernel and the octet which the manganese atom holds in common with the 4 oxygen atoms. If the structure of manganese is regarded as invariable, divalent salts, such as manganous chloride, present even greater difficulties. Such a compound would be formed by one electron passing

from the outer layer of the manganese atom to each of the two chlorine atoms, leaving 5 free electrons in the outer shell of the manganese atom. No octet is formed round the manganese atom in which these 5 could be held prisoner. Free electrons in the outer shell of an atom cause a substance containing that atom to be highly reactive, yet manganous salts are probably the most stable compounds of manganese.

Lewis<sup>2</sup> in his hypothesis of the cubical atom expresses the opinion that in these elements "the kernel of the atom is not uniquely and permanently defined." In his magneton theory of the structure of the atom, Parson<sup>3</sup> uses the conception of "tautomerism" in the structure of the atom to account for the structure of the elements of the first long period.

The remaining elements of this period have their 3 inner shells complete. Zinc will have the structure (2,8,18,2): there is no possibility of change of structure, and it is therefore a normal element and resembles magnesium and glucinum, the two normal elements of lower atomic weight that have two electrons in the outer layer. Each succeeding element in the period will have one more electron in the fourth shell. Krypton will have the structure (2,8,18,8) and, like argon, owes its chemical properties to the stability of the group of 8 in the outer layer, although this fourth layer is unsaturated, for it can hold 32 electrons.

**The Second Long Period.**—The chemical properties of this group seem to indicate that the groups of 8 and 18 electrons in the fourth layer are more stable than they were in the third.

Rubidium (2,8,18,8,1), strontium (2,8,18,8,2), and yttrium (2,8,18,8,3) are analogous to potassium, calcium and scandium. A fifth layer is being built over an incomplete fourth shell.

The electrons in the outer layers of zirconium, columbium and molybdenum show little tendency to pass into the inner layers. Their chemical properties, so far as they are known, seem to be explained by one structure only for each element, (2,8,18,8,4), (2,8,18,8,5) and (2,8,18,8,6), respectively. In this they differ from the elements preceding them in their respective groups, titanium, vanadium and chromium. Those compounds in which they exhibit their highest valence are relatively more numerous, and in these alone do they resemble the elements of the first long period. The divalent salts of molybdenum, which are probably complexes of more elaborate constitution than their simple empirical formulas would suggest, are very different from the divalent salts of the transition elements of the first long period. Molybdates have not the same oxidizing properties that the chromates have.

No element of atomic number 43, corresponding to manganese, has as yet been discovered.

<sup>2</sup> Lewis, *THIS JOURNAL*, 38, 785 (1916).

<sup>3</sup> Parson, *Smithsonian Misc. Coll.*, 65, No. 11, p. 23 (1915).

The fact that ruthenium forms a tetroxide, in which it must have the structure (2,8,18,8,8), shows that in this period the electrons pass into the inner layer less readily than in the first long period, for iron shows no sign of having a similar structure.

Again, possibly owing to the greater stability of the group of 18 electrons in the fourth shell, silver forms only monovalent salts, in which it must have the structure (2,8,18,18,1); unlike copper, it shows no tendency to form divalent salts in which it would have the structure (2,8,18,17,2). This causes the process of transition from a group of 8 to one of 18 electrons in the fourth shell to be much shorter, and to be more sudden than it was in the third shell. In the first long period, there were 8 transition elements; in the second long period there are only 3, ruthenium, rhodium and palladium; and these show but little resemblance to their analogs in the first long period, iron, cobalt and nickel. As transition elements, they may have different structures in their different compounds, and the following possibilities can be recognized:

Ru (2,8,18,8,8) (2,8,18,9,7) (2,8,18,10,6) (2,8,18,12,4) (2,8,18,13,3) (2,8,18,14,2)  
 Rh (2,8,18,11,6) (2,8,18,13,4) (2,8,18,14,3) (2,8,18,15,2)  
 Pd (2,8,18,14,4) (2,8,18,15,3) (2,8,18,16,2)

As in the previous transition series in the first long period, the lower valences of the first transition elements lead to the formation of unstable compounds; ruthenium and rhodium divalent salts are unstable. The last transition element, palladium, shows the same preference for the lower valences that is characteristic of cobalt and nickel; palladium trioxide and its derivatives are unknown, and palladium alone, of this series, forms stable divalent salts. In this transition series, it is a rule, not without exceptions, that those structures that contain an even number of electrons in the fourth shell lead to the formation of the most stable compounds.

Silver has the structure (2,8,18,18,1): the fourth shell is still incomplete, for it can contain 32 electrons. It nevertheless contains a stable group of 18. This stable but incomplete group of 18 electrons in the fourth shell remains to the end of the second long period, each succeeding element having one more electron in the fifth layer. It is possible that such compounds as cadmous oxide ( $\text{Cd}_2\text{O}$ ), indium dichloride, and the stannous salts might be ascribed to electrons passing from the fifth to the incomplete fourth layer, but no such possibility can account for the existence of gallium and germanium dichlorides. The last elements of this period form compounds by completing the octet in the fifth layer; and the transition from 18 to 32 electrons in the fourth shell does not occur till the next period.

Xenon will have the structure (2,8,18,18,8).



**The Rare Earth Period.**—Cesium, barium and lanthanum will have the structures (2,8,18,18,8,1), (2,8,18,18,8,2) and (2,8,18,18,8,3) respectively, a sixth layer being built over incomplete but stable groups of 18 and 8 electrons in the fourth and fifth shells.

0 1 2 3 4 5 6 variable										3 4 5 6 7 variable										1 2 3 4 5 6 7 8										TRANSITION METALS 111																			
H																				He O										SUCCESSIVE SHELLS OF ATOM!																			
He Li																				Be B C N O F Ne 2																													
Ne Na																				Mg Al Si P S Cl Ar 2, 8																													
Ar K Ca										Sc																				2, 8, 8																			
										(V V Cr Mn Fe Co Ni Cu)																				variable 1st 8-18 transition series																			
Mn Re Se										Y Zr Nb Mo 4f										2n Ga Ge As Se Br Kr										2, 8, 18																			
										(R, Rh Pd)																				variable 2nd 8-18 transition series																			
Xe Cs Ba La																				Ac Cd In Sn Sb Te I Xe										2, 8, 18, 18																			
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										Lv 72 Ta W 75																				variable 3rd 8-18 transition series																			
										(Xr In Pt Au)																				2, 8, 18, 32, 18																			
At 87 Ra Ac Th 90 U																				Hg Tl Pb Bi Po 84										2, 8, 18, 32, 18																			

Periodic arrangement of the elements and structure of their atoms. No attempt to represent the variable structures of the four transition series has been made.

Cerium is the first of a transition series in which the group of 18 electrons in the fourth layer is changed to one of 32. In previous transition series, succeeding elements have differed in similar compounds only by one electron in the outer shell of their kernels: in this series they will differ only by one electron in an inner shell, the fourth, of their kernels. The elements will therefore resemble each other in similar compounds even more closely than, for example, manganese, iron, cobalt, nickel and copper in their divalent salts. A second feature of this transition series is that the elements do not show that variety of structure that is found in other transition series, though a few elements show signs of having more than one structure. The following structures are suggested.

Ce	(2,8,18,18,8,4)	(2,8,18,19,8,3)
Pr	(2,8,18,19,8,4)	(2,8,18,20,8,3)
Nd	(2,8,18,21,8,3)	
Undiscovered element of atomic number 61.		(2,8,18,22,8,3)
Sa	(2,8,18,23,8,3)	(2,8,18,24,8,2)
Eu	(2,8,18,24,8,3)	(2,8,18,25,8,2)
Gd	(2,8,18,25,8,3)	

So far as their chemical properties are known, the remaining seven rare earths show no sign of having more than one structure. Each succeeding element will have one more electron in the fourth shell. Lutecium, the rare earth of highest atomic weight, will have the structure (2,8,18,32,8,3); the fourth shell is now complete, and it will be a normal element. Lutecium, rather than lanthanum (2,8,18,18,8,3), resembles scandium (2,8,8,3) and yttrium (2,8,18,8,3), just as, in the first long period, zinc rather than calcium resembles glucinum and magnesium.

Between lutecium and tantalum an element of atomic number 72 is to be expected. This would have the structure (2,8,18,32,8,4), and would resemble zirconium.

Tantalum and tungsten have the structures (2,8,18,32,8,5) and (2,8,18,32,8,6), and are analogous to columbium and molybdenum. An element of atomic number 75 remains undiscovered.

Osmium, iridium, platinum and possibly gold form a transition series in which the group of 8 in the fifth layer changes to a group of 18 electrons. This third 8-18 transition resembles the second, rather than the first, such transition; and in fact, osmium, iridium, and platinum, resemble ruthenium, rhodium and palladium more than they resemble iron, cobalt and nickel. The various structures which these elements, as transition elements, can assume are probably as follows.

Os (2,8,18,32,8,8) (2,8,18,32,10,6) (2,8,18,32,12,4) (2,8,18,32,13,3) (2,8,18,32,14,2)  
 Ir (2,8,18,32,11,6) (2,8,18,32,13,4) (2,8,18,32,14,3) (2,8,18,32,15,2)  
 Pt (2,8,18,32,12,6) (2,8,18,32,14,4) (2,8,18,32,15,3) (2,8,18,32,16,2)  
 Au (2,8,18,32,16,3) (2,8,18,32,17,2) (2,8,18,32,18,1)

In this transition series also, the first elements have a tendency to form compounds with the highest valences, and the last elements to form compounds with the lower valences. Those compounds in which the metal has an even number of electrons in its fifth shell are generally more stable than when the number of electrons in the fifth layer is odd.

Mercury will have the structure (2,8,18,32,18,2), the 4 inner shells being complete, the fifth containing an incomplete but stable group of 18 electrons. Each succeeding element in this period will have one more electron in the sixth layer, until we come to niton, with the structure (2,8,18,32,18,8).

**The Last Period.**—Only 5 elements of this period are known, and the chemical properties of only two of them, thorium and uranium, are known well. In this period a second 18-32 transition series may be expected.

The second 8-18 transition series was shorter and more sudden than the first, possibly because of the greater stability of the groups of 8 and 18 electrons in the fourth, than in the third shells; and the elements of the second transition series showed but little resemblance to those of the first. To judge by analogy, the second 18-32 transition series may be expected to begin later, to end earlier, to be shorter and more abrupt than the first 18-32 transition series. Little resemblance between the chemical properties of the elements of the two series is to be expected. Possibly an element, not yet discovered, of atomic number 94, two more than that of uranium, is the first of a series of 7 transition elements that would be metals, something like the ruthenium group but more electropositive. Possibly uranium itself is the first member of this second 18-32 transition

series. The following structures are suggested for the elements of this period.

Ra	(2,8,18,32,18,8,2)	Th	(2,8,18,32,18,8,4)
Ac	(2,8,18,32,18,8,3)	Ux <sub>2</sub>	(2,8,18,32,18,8,5)
	U	(2,8,18,32,18,8,6)	

The structures for the elements arrived at are more in harmony with the atomic diameters, determined by Bragg<sup>4</sup> from the study of crystal structure, than are the structures given by Langmuir.

Element.	Atomic diameter in Å. (Bragg).	Number of shells in kernel. (Langmuir). (Bury).	
Lithium.....	3.00	1	1
Sodium.....	3.55	2	2
Potassium.....	4.15	2	3
Rubidium.....	4.50	3	4
Cesium.....	4.75	3	5
		Number of shells in atom.	
Fluorine.....	1.35	2	2
Chlorine.....	2.10	2	3
Bromine.....	2.38	3	4
Iodine.....	2.80	3	5

On the basis of Langmuir's structures for the elements, the difference in atomic diameter between rubidium and potassium might be expected to be more than that between potassium and sodium, for both the latter contain 2 shells of electrons, while rubidium contains 3. On the basis of the atomic structures suggested in this paper, the difference in atomic diameters between any two successive elements in the same group might be expected to be constant.

During the course of preparation of this paper, structures similar to those suggested by the author for the inert gases have been proposed by Bohr,<sup>5</sup> who bases his arguments on the study of emission spectra.

### Summary.

An alternative to Langmuir's fourth postulate, in his paper on the arrangement of electrons in atoms and molecules, has been suggested. This avoids the necessity of postulating cells in the structure of the atom, and leads to different structures for the elements of higher atomic weight than neon. It is claimed that the application of Lewis and Langmuir's octet theory of valence to these structures gives a better explanation of the chemical properties of the higher elements, than can be obtained from Langmuir's structures.

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<sup>4</sup> Bragg, *Phil. Mag.*, [6] 40, 169 (1920).

<sup>5</sup> Bohr, *Nature*, 107, 106 (1921).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE VOLUMETRIC DETERMINATION OF SULFIDE BY  
OXIDATION TO SULFATE.

BY H. H. WILLARD AND W. E. CAKE.

Received April 28, 1921.

In the usual iodometric oxidation of hydrogen sulfide to sulfur only two equivalents of oxygen are required, whereas if it is oxidized to sulfuric acid, eight equivalents are necessary. It would obviously be a distinct advantage to use the latter process instead of the former, if it could be as readily accomplished. Of the methods suggested for this purpose only three can be considered as reasonably accurate. Feit and Kubierschky<sup>1</sup> added to the sulfide excess of standard bromate solution, acidified with sulfuric acid, boiled off the bromine liberated in the reaction and titrated the excess of bromate iodometrically. Dean<sup>2</sup> oxidized hydrogen sulfide with a large excess of standard iodate solution in a solution containing sufficient hydrochloric acid to form iodine chloride and titrated the excess with standard *iodide* solution. Kolthoff<sup>3</sup> added an excess of standard bromine solution and determined the excess iodometrically. The first and last methods have several obvious disadvantages and the second one requires a high concentration of hydrochloric acid, which is somewhat inconvenient, since alkaline solutions must be used to absorb hydrogen sulfide. In connection with the use of hypobromite in the determination of ammonia<sup>4</sup> it seemed desirable to investigate the use of this reagent (and also hypochlorite) for the oxidation of sulfide to sulfate. It was found that if the solution is sufficiently alkaline the oxidation goes very rapidly according to the equation,  $4 \text{NaBrO} + \text{Na}_2\text{S} = 4 \text{NaBr} + \text{Na}_2\text{SO}_4$ . The excess of hypobromite is easily determined by adding potassium iodide, acidifying, and titrating the liberated iodine by means of thio-sulfate. The same reaction occurs with hypochlorite, but less readily.

## Preparation of the Standard Hypobromite Solution.

A solution of convenient concentration was prepared by adding 100 g. of bromine slowly and with constant stirring to a solution of 60 g. of pure sodium hydroxide in 1600 cc. of water, keeping the solution well cooled. Such a solution is about 0.6 *N* and 1 cc. corresponds to approximately 2.4 mg. of sulfur. Since the presence of traces of iron, copper and other metals increases enormously the rate of decomposition of the solution, it is advisable to let the hydroxide solution stand for a day or two and filter or siphon off the clear liquid, before adding the bromine. It should be kept in the dark; but even with pure materials the rate of decomposition is appreciable.<sup>4</sup> Fleury<sup>5</sup> has shown that this

<sup>1</sup> Feit and Kubierschky, *Chem. Ztg.*, **15**, 351 (1891).

<sup>2</sup> Dean, *THIS JOURNAL*, **40**, 619 (1918).

<sup>3</sup> Kolthoff, *Pharm. Weekblad*, **56**, 143 (1919).

<sup>4</sup> Willard and Cake, *THIS JOURNAL*, **42**, 2646 (1920).

<sup>5</sup> Fleury, *Compt. rend.*, **171**, 957 (1920).

may be greatly decreased by adding to each liter of solution 1 g. of potassium iodide or iodate. This suggestion was tried, with contradictory results. One solution changed rapidly to bromide and bromate, the total oxygen remaining unchanged. Another, more dilute in hypobromite but containing relatively more alkali, showed almost no change. The reason for this difference in behavior is being investigated.

#### Preparation of the Standard Hypochlorite Solution.

A hypochlorite solution made from sodium hydroxide purified as described above is much more stable. It was prepared by passing into a cold solution of 90 g. of sodium hydroxide in 1500 cc. of water sufficient dry chlorine to give an increase in weight of about 35 g. Table I shows the rate of change of this solution when kept in the dark at about 22°.

TABLE I.

Date.	Cc. of 0.1 <i>N</i> thiosulfate sol. equivalent to 10 cc. of hypochlorite sol.
Nov. 7	69.16
8	69.06
12	68.96
26	68.67
Dec. 3	68.34
8	68.18
25	67.57

#### Procedure.

In the experiments described the procedure was as follows. To the alkaline sulfide solution was added sufficient standard hypobromite or hypochlorite solution so that not over two-thirds of it was reduced by the sulfide. After standing for 3 to 5 minutes, 2 to 3 g. of potassium iodide was added and the solution diluted to 4 or 5 times the original volume. The solution was neutralized with conc. hydrochloric acid (the color of the iodine acts as an indicator) and 3 to 5 cc. in excess was added. The iodine was then titrated with standard thiosulfate solution.

#### Effect of Varying the Concentration of Sodium Hydroxide.

Unless a certain minimum concentration of sodium hydroxide is present the oxidation is incomplete. This is shown in Table II. To 50 cc. of sodium hydroxide solution of the concentration given were added 5 cc. of standard sodium sulfide solution and 10 cc. of standard hypobromite or hypochlorite solution; the excess was titrated as described above. The theoretical value as determined by an iodine titration is 9.86 cc.

TABLE II.

Conc. of NaOH solution. <i>N</i> .	Cc. of NaClO reduced.	Cc. of NaBrO reduced.
1	7.05	8.11
2	9.45	9.50
3	9.68	9.82
4	9.73	9.82
5	9.83	9.86
6	9.85	9.86

It was found, using 2 *N* sodium hydroxide solution, that, in the case of hypochlorite, heating to 45° for 5 minutes reduced the error a little, but standing for 30 minutes at room temperature had no effect. From this it is evident that, when using hypobromite, the concentration of sodium hydroxide during the reaction must be at least 2.5 *N* and when using hypochlorite, 4 *N*. Practically, therefore, only hypobromite would be used, but experiments were made with both reagents.

The first experiments were made with a solution of sodium sulfide prepared by absorbing about 2 g. of hydrogen sulfide in 16 g. of sodium hydroxide dissolved in a liter of water. Ten cc. of this solution was pipetted into a flask, 10 cc. of 10 *N* sodium hydroxide solution added, then 20 cc. of standard hypobromite solution. After standing for 5 minutes 100 cc. of water was added and 3 g. of potassium iodide. The solution was acidified with conc. hydrochloric acid, 5 cc. in excess being added. The iodine was titrated with thiosulfate. The results are shown in Table III.

TABLE III.

S found. G.	S present by iodine titration. G.
0.0193	0.0195
0.0195	.....
0.0194	.....
0.0195	.....
0.0196	.....

The same procedure was followed, using hypochlorite, except that twice as much sodium hydroxide was added. Another solution of sodium sulfide was used.

TABLE IV.

S found. G.	S by iodine titration. G.
0.0150	0.0150
0.0151	.....
0.0150	.....

This method was found to be rapid and accurate for the determination of sulfur in steel. The steel was dissolved in hydrochloric acid in the usual way, the hydrogen sulfide absorbed in sodium hydroxide and titrated as described above. The other gases, such as hydrocarbons and phosphine, either were not absorbed or did not reduce the oxidizing solution.

#### Procedure for Steels.

Weigh out 5 g. of the steel into a 250-cc. flask through which hydrogen can be passed and which is connected with a "10-bulb tube" for absorbing the hydrogen sulfide. Flush out the apparatus with hydrogen and run into the flask 100 cc. of hydrochloric acid (sp. gr. 1.1). After the reaction has moderated heat the solution just to boiling for 5 minutes after the steel

has dissolved, while passing hydrogen through the apparatus. The solution in the absorption tube should contain about 6 or 7 g. of sodium hydroxide in a volume of 50 to 60 cc. With as little water as possible wash the contents of the bulbs into a flask containing 10 cc. of 0.3 *N* hypobromite solution, let stand for 3 to 4 minutes, add 2 to 3 g. of potassium iodide in solution, dilute to 150 cc., add conc. hydrochloric acid till neutral, and then 5 cc. more. Titrate the iodine with 0.1 *N* thiosulfate solution. If hypochlorite is used more sodium hydroxide must be added.

**Precautions.**—If the solution is not sufficiently alkaline, oxidation will be incomplete.

The solution when neutralized must be kept cool enough to avoid volatilization of iodine.

Low results will be obtained unless the apparatus is flushed out with hydrogen.

Table V shows the results obtained by this procedure. 10 cc. of hypobromite solution was used in all determinations except those marked with an asterisk, in which hypochlorite was used.

TABLE V.

No. of Expt.	Description of steel.	Weight. G.	S found. %.	S present by certif.
1	0.1% C	5.0018	0.080	0.080
2*	"	5.0000	0.080	.....
3*	"	5.0000	0.081	.....
4	1% C.	5.0001	0.026	0.028
5	"	5.0020	0.027	.....
6*	0.2% C.	5.0057	0.026	.....
7	30	5.0044	0.031	0.033
8	"	5.0000	0.032	.....
9	32	5.0040	0.025	0.024
10	33	5.0022	0.028	0.028
11*	"	5.0000	0.027	.....
12*	"	5.0000	0.028	.....

### Procedure for Sulfides.

If the sulfide is soluble in hydrochloric acid, no preliminary treatment is required. Insoluble sulfides are first ignited with powdered iron (reduced by hydrogen) free from sulfur, in an atmosphere of hydrogen or carbon dioxide, the ferrous sulfide<sup>6</sup> thus formed being soluble in acids. The sample is treated in the same way as described for steels, except that 0.6 *N* hypobromite and 0.2 *N* thiosulfate solutions are more convenient, and the volume of the former must be increased according to the amount of sulfide present. Table VI shows the results obtained with samples of zinc and cadmium sulfides and mixtures of the two. Hypochlorite was used in Expts. 3 and 4. In Expts. 11 and 12 the sulfide was first

<sup>6</sup> Zehetmayer, *Z. angew. Chem.*, 23, 1359 (1910).

ignited with powdered iron, and the slightly higher value obtained is due to reduction of a small amount of sulfate which was present.

TABLE VI.

Expt.	Description of sample	Wt. of sample.	NaBrO added.	S found.	S found by
		G.	Cc.	%.	iodine titration.
1	CdS	0.1328	20	21.17	21.00
2	CdS	0.1520	20	20.97	.....
3	CdS	0.1078	20	21.01	.....
4	CdS	0.1026	20	21.15	.....
5	ZnS	0.3714	60	32.02	32.00
6	ZnS	0.3024	50	32.05	.....
7	{ Mixture A } CdS+ZnS Mixture B CdS+ZnS	0.0856	20	23.56	23.65
8		0.2692	50	23.67	.....
9		0.1256	30	29.96	29.90
10		0.1830	30	29.92	.....
11	CdS	0.1456	40	21.43	21.45
12	CdS	0.1892	50	21.50	.....

The method may be applied to the direct oxidation of precipitated sulfides, but not natural sulfides. Zinc, mercuric and antimony sulfides were found to react readily with hypobromite and probably all others would do so. If free sulfur or polysulfide is also present, as is often the case, this too will be oxidized, although it has no effect in the iodine method.

It should be emphasized that all other reducing agents, ammonia for example, must be absent, since many substances not oxidized by iodine are oxidized by hypobromite.

#### Summary.

1. Sulfide is rapidly and completely oxidized to sulfate by excess of hypobromite in a solution 2.5 *N* with sodium hydroxide or by hypochlorite in a 4 *N* solution. The excess of oxidizing agent is determined iodometrically. Four times as much oxygen is required as in the usual titration with iodine.

2. The method gives accurate results in the determination of sulfur in steels and in sulfides, if care is taken to exclude all other reducing agents.

ANN ARBOR, MICH.



[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO.]

## ADSORPTION OF RADIUM BY BARIUM SULFATE.

BY FRANK E. E. GERMANN.

Received May 2, 1921.

The study of the laws of adsorption is usually restricted to those substances which adsorb appreciable masses of material. It is on this account that charcoal is used to such a large extent. The reason for this limitation is that our analytical methods cannot be used to detect the difference in concentration of a solution caused by adsorbents that are not very active. As a result, our knowledge of adsorption phenomena is restricted to a rather limited region.

The case of the adsorption of a radio-active substance by a solid is an exception to the usual type, as in this case we have methods of measurement available other than the usual analytical methods. In the case of the emanation method of the analysis of the radium content of a solution, it is a simple matter to obtain an accuracy of 2 to 5%, where the total radium content is much less than one part per billion.

If radium-free barium sulfate be added to a standard solution of radium barium chloride, a certain quantity of the radium will be adsorbed by the sulfate. After equilibrium has been established, the sulfate can be filtered off and the residual radium in the solution determined. We thus have an ideal method for the study of the laws of adsorption which is applicable to the adsorption of masses which lie far below the quantities which could be determined analytically. The accuracy of the method is all that could be desired.

The study of this particular case is of considerable importance in the commercial refining of radium. Commercial hydrochloric acid contains appreciable quantities of soluble sulfates, which must be precipitated by means of barium chloride before the acid is used to dissolve the carbonates carrying the radium. If the barium sulfate is allowed to settle and the clear acid decanted as used, it may happen at times that traces of the insoluble sulfate are carried over with the acid. The question then arises as to the possible harm that this could do in the extraction of the radium from the carbonate. If the acid-insoluble "tails" run high in radium, how much of this should be attributed to the presence of barium sulfate? It was with these problems in view that the following investigation was undertaken.

A solution of radium barium chloride in approximately *N* hydrochloric acid was made up, and, after standing for several days, was standardized, as far as the radium content was concerned, by means of 3 samples, sealed for a month. When the emanation had reached equilibrium, it was boiled off in the usual way and the radium content of the solution determined.

The average of these 3 determinations showed a radium content of  $22.79 \times 10^{-10}$  g. of radium per cc. of solution.

The barium sulfate was prepared by adding sulfuric acid to a dilute solution of pure barium chloride while boiling. Prepared under these conditions, the sulfate settled readily, and could easily be washed by decantation to rid the precipitate of the sulfuric acid. The barium sulfate was then filtered off, dried, and ignited in a muffle for several hours to remove any residual traces of acid. After cooling, it was pulverized in an agate mortar and passed through a 200-mesh sieve in order to have greater uniformity in the size of the particles.

Ten cc. of the standard radium solution was then diluted to 80 cc. and 0.05 g. of barium sulfate added. The mixture was then boiled for about 20 hours, under a reflux condenser. Experience showed that equilibrium is not reached in 10 hours, but that boiling longer than 18 hours produced no further change in the mass adsorbed. After the adsorption equilibrium had been established, the barium sulfate was filtered off and the solution sealed and set away for a month prior to the emanation determination. Similar runs were made on the same volume of standard solution with varying masses of barium sulfate. Making all the runs under similar conditions, the final volumes of the solutions at equilibrium were the same, and hence the conditions were comparable. The results are tabulated below. Ten cc. of standard solution was used in all experiments.

Expt.	BaSO <sub>4</sub> G.	Ra/cc. at equil. $\times 10^{10}$ G.
1	0	21.86
2	0	23.62
3	0	22.89
4	0.05	18.55
5	0.10	15.08
6	0.10	15.15
7	0.20	8.45
8	0.20	10.48
9	0.30	5.86
10	0.40	3.97
11	0.50	2.70

In addition to the above experiments, one blank was made up with all of the reagents except the standard radium solution. No activity was obtained from this test run, which served as a guarantee that the substances used were all free from radium with the exception of the standard radium solution.

According to the experimental work of Kroeker<sup>1</sup> on adsorption, we may write

$$\left( dx = \lambda \frac{a-x}{v} dm \right) \quad (1)$$

<sup>1</sup> Kroeker, Thesis, Berlin, 1892.

where  $x$  represents the mass adsorbed,  $a$  the total mass initially dissolved,  $v$  the volume of the solution,  $m$  the mass of the adsorbent, and  $\lambda$  a constant. On integrating the above expression, we obtain the equation

$$\lambda = v/m \ln \left( \frac{a}{a-x} \right) \quad (2)$$

Since  $x$  represents the mass adsorbed,  $(a-x)$  would represent the concentration of the solution after adsorption equilibrium had been established, provided the volume  $v$  be taken as unity. Under these conditions, let  $(a-x)$  be designated by  $y$ . Our equation becomes

$$\begin{aligned} \lambda &= 1/m \ln a/y \text{ or} \\ \ln y &= -m \lambda + \ln a \end{aligned} \quad (3)$$

which, written in the exponential form would be

$$y = a e^{-m\lambda} \quad (4)$$

According to Equation 3 it is evident that any case of true adsorption would give us a straight line curve if we plot  $\log y$  as ordinates against mass  $m$  as abscissas. Curve I shows this to be the case.

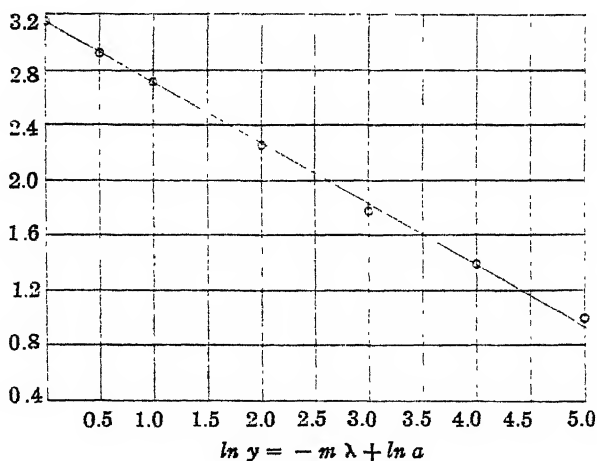


Fig. 1.

If we admit with Freundlich<sup>2</sup> that

$$\lambda = v/m \ln \frac{a}{a-x} = \alpha \left( \frac{a}{s} \right)^{-1/n} \quad (5)$$

in which  $\alpha$  and  $n$  are constants depending only on the temperature and the nature of the dissolved substance, it can be shown that the usual form of the adsorption isotherm

$$x/m = \beta c^{1/p} = \beta \left( \frac{a-x}{s} \right)^{1/p} \quad (6)$$

<sup>2</sup> Freundlich, *Z. physik. Chem.*, 57, 395 (1906).

can be derived from 5 by expanding the two sides of the equation in series and neglecting all but the first term of each series. The term  $c$  is the concentration of the solution at equilibrium. Writing Equation 6 in the logarithm form, we obtain

$$\ln x/m = 1/p \ln c + \ln \beta \quad (7)$$

which shows that if we plot the logarithms of the ratio of the mass adsorbed to the adsorbing mass ( $\log^* x/m$ ) against the logarithm of the equilibrium concentration, we should have a straight line. Curve II shows that this is borne out by experiment.

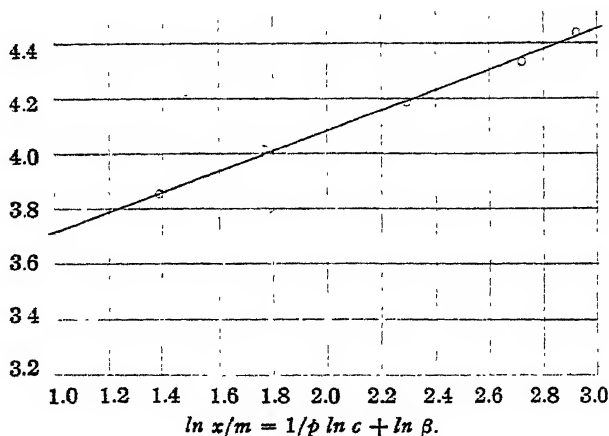


Fig. 2.

The usual procedure in adsorption work has been to use some such substance as blood charcoal, which adsorbs large quantities of material. Thus, in one set of experiments due to Freundlich, acetic acid and blood charcoal being used, the concentration of acid varied from 0.02 to 2.80  $N$ , while the mass adsorbed per gram of charcoal varied between 0.028 and 0.226 g. In the experiments recorded in the present article, we are dealing with altogether different orders of magnitude. The concentration of radium chloride adsorbed per gram of adsorbent ( $\text{BaSO}_4$ ) was of the order of  $5 \times 10^{-8}$ . No doubt the barium chloride was also being adsorbed, but this would be of no consequence as far as the radium adsorption is concerned. It thus appears that the same laws of adsorption apply to these minute quantities of radium that apply to the adsorption of ponderable masses of ordinary chemical substances.

When a radium barium chloride solution is incompletely precipitated by means of a soluble sulfate, such as sulfuric acid, the radium and barium come down in about the same proportion as they exist in the original solution, there being a slight concentration of the radium in the precipi-

tate. In other words, very little concentration of radium can be effected by a fractional precipitation method. Since the solubility of pure radium sulfate in water is so great that there could be no thought of a precipitation in the case of concentrations met with in the working up of radium ores, we are in the habit of speaking of the phenomenon of barium and radium precipitating together as adsorption. Looking at the question from the point of view of solubility product considerations, we could about as well explain the precipitation of the radium from the point of view of a salting out process which is brought about by the great excess of sulfate ions belonging to the dissolved barium. The fact that the adsorption law is followed in the case of the radium chloride would lead one to favor the adsorption theory in the case of a precipitation of the sulfate.

If we admit the validity of the adsorption theory in the case of a precipitation, the question arises as to why we can get a complete extraction of radium by means of a complete barium precipitation, whereas in the case of barium radium chloride in contact with barium sulfate we have an equilibrium radically different from what would be expected on the basis of the barium in solution compared to the barium present as sulfate. Thus 10 cc. of the standard solution contained about 0.04 g. of barium chloride. This solution, in contact with 0.05 g. of barium sulfate (of almost the same molecular weight as the radium sulfate) came to equilibrium with  $\frac{4}{5}$  of the radium adsorbed on 0.04 g. or about half of the barium. Again 0.04 g. of barium chloride in the solution in equilibrium with 0.5 g. of barium sulfate came to equilibrium with  $\frac{1}{7}$  of the radium adsorbed on  $\frac{1}{12}$  of the barium. Evidently this is something more than just a proportionate distribution of the radium with the barium.

A better understanding of these phenomena can be obtained if we consider for a moment the adsorption equation as modified by Freundlich.

$$x/m = \alpha c^{1/n} \quad (8)$$

where  $x$  and  $m$  have the same significance as before and  $c$  is the concentration at equilibrium, or  $\frac{a-x}{v}$ . The term  $m$  represents the mass of the adsorbent, and is used as a measure of the surface area of the adsorbent, to which it bears a definite relation, in the case of an adsorbent of given fineness. Hence the term  $x/m$  is in a way a measure of mass adsorbed per unit area of adsorbent. The constants  $\alpha$  and  $n$  are as mentioned above dependent only on the temperature and the nature of the dissolved substance. When we mix barium sulfate with a solution of barium radium chloride of known concentration, the area of the adsorbent is comparatively small. Since the concentration  $c$  is small and the area is small, the term  $x$  or the mass adsorbed will be finite. If on the other hand we precipitate barium sulfate from a solution of barium radium chloride, the area of

the adsorbent is tremendous, as the precipitate grows from about molecular dimensions. When the area becomes very large,  $\alpha$  must also become large in order to keep  $c$  finite. The result is a complete precipitation of the radium with the barium. If these considerations are valid, we might expect to be able to precipitate all of the radium before all of the barium has been thrown down. In other words we might expect to be able to carry on a fractional precipitation. This does not seem to be the case with radium, but it may be noted that it can be done with certain radio-active substances.<sup>3</sup> In this connection it is well to remember that adsorption is a specific property, depending not only on the adsorbent and the adsorbed substance, but also on the solvent.

We may make the above considerations clear by means of the following crude calculations. Let us assume that the diameter of the molecule is of the order of  $10^{-8}$  cm. Its area, assuming it to be spherical, would be about  $3 \times 10^{-16}$  sq. cm. There would be approximately  $10^{24}$  molecules per cc. of substance if we can assume close packing. Hence 1 cc. of solid substance of molecular sized particles would present an area of  $10^{24} \times 3 \times 10^{-16}$ , or  $3 \times 10^8$  sq. cm.

Now suppose we take the precipitated barium sulfate which was put through a 200-mesh sieve. Assuming the wire to have the same diameter as the hole, we would have holes 0.006 cm. square. Particles smaller than this also pass through. Let us therefore suppose, for the sake of argument, that the average particle passing through has a diameter of 0.002 cm. Its radius will be 0.001 cm., and its area approximately  $10^{-5}$  sq. cm. Of these particles there would be about  $10^8$  per cc. of solid substance, giving us a total area of  $10^8 \times 10^{-5}$ , or  $10^3$  sq. cm. We thus see that we have 1000 sq. cm. in the latter case as compared to three hundred million in the former. The former is three hundred thousand times the latter.

Regarding Equation 7 in the light of these figures we can readily see that  $\alpha$  must approach as a limiting value the total mass of substance dissolved which is capable of being adsorbed. As the area of the adsorbent (a number proportional to  $m$  in the general case) becomes very large, the concentration  $c$  must approach zero.

### Summary.

1. The adsorption law of Kroeker has been experimentally tested in the case of a radio-active substance and found to hold true.
2. The adsorption law of Freundlich has been experimentally tested and found to hold true in the case of a radio-active substance.
3. The same laws of adsorption which apply to the adsorption of ponderable masses are found to apply with an equal degree of accuracy to masses of  $5 \times 10^{-8}$  g. adsorbed per gram of adsorbent.

<sup>3</sup> Unpublished work of the author.

4. The relationship existing between adsorption taking place during precipitation, and that taking place on a solid precipitate of definite surface area has been discussed.

BOULDER, COLORADO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE SURFACE TENSIONS AND DENSITIES OF LIQUID MERCURY, CADMIUM, ZINC, LEAD, TIN AND BISMUTH.

By THORFIN R. HOGNESS.<sup>1</sup>

Received May 6, 1921.

The purpose of this investigation was to secure data for the examination of metallic solutions from the standpoint of the theory of solubility which has been outlined by Hildebrand and extensively applied by him and his co-workers<sup>2</sup> to non-metallic solutions. Although surface tension has proved to be a criterion of great value with non-metallic solutions, the evident inaccuracy of much of the data heretofore published upon the surface tensions of liquid metals has made the work herein described prerequisite to the accomplishment of the above purpose.

The method selected for our purpose is one originated by Cantor<sup>3</sup> and extensively applied by Jaeger<sup>4</sup> to non-metallic liquids. The method as it is generally employed consists in determining the pressure necessary to force a bubble of inert gas from the end of a sharp edged platinum capillary immersed in the liquid. On account of the impossibility of using a metallic capillary with liquid metals the process has been reversed in the present work so as to measure the pressure necessary to force a tiny drop from the tip of a quartz capillary directed upwards. The theory of this method is as follows.

The free surface energy of a sphere of liquid of surface  $s$  and surface tension  $\gamma$  is  $\gamma s$ . If the drop is increased infinitesimally in size by introducing more liquid, say, through a fine capillary, the work done against the surface tension is  $\gamma ds$ . This is equal to the pressure exerted by the tension upon the interior of the drop multiplied by the increase in volume  $dv$ , so that  $\gamma ds$  equals  $p dv$ . Since  $s = 4\pi r^2$  and  $v = \frac{4}{3}\pi r^3$ , we have  $\gamma = pr/2$ .

If we have a small capillary of radius  $a$  and apply pressure to force out a drop of the liquid, the radius of curvature of the drop will gradually

<sup>1</sup> Thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Hildebrand, *This Journal*, 38, 1452 (1916); 39, 2297 (1917); 41, 1067 (1919); 43, 500 (1921). Hildebrand and Jenks, *ibid.*, 42, 2180 (1920). Hildebrand and Buehrer, *ibid.*, 42, 2213 (1920).

<sup>3</sup> Cantor, *Wied. Ann.*, 47, 399 (1892).

<sup>4</sup> Jaeger, *Z. anorg. Chem.*, 101, 1 (1917).

diminish as the pressure increases until it reaches a minimum value where  $r$  equals  $a$ . At this point the corresponding pressure will be a maximum, and it is this maximum pressure that is measured. The force of gravity causes a slight distortion of the drop necessitating a correction for the larger capillaries. This distortion is accounted for in the formula derived by Cantor, and corrected by Feustel,<sup>5</sup> where  $d$  is the density of the liquid.

$$= \frac{pa}{2} \left( 1 - \frac{2}{3} \frac{da}{p} - \frac{d^2 a^2}{p^2} \right)$$

This method has marked advantages over most others applicable to the metals in that it provides for a fresh and uncontaminated surface; it avoids the introduction of contact angle, which is necessary in the capillary depression method; it depends only upon primary standards; and it is free from theoretical uncertainties such as are involved in the drop-weight method.

### Description of Apparatus.

The apparatus finally adopted is shown in Fig. 1. The whole apparatus was built of Pyrex glass, with the exception of A which is a quartz capillary. The capillary was

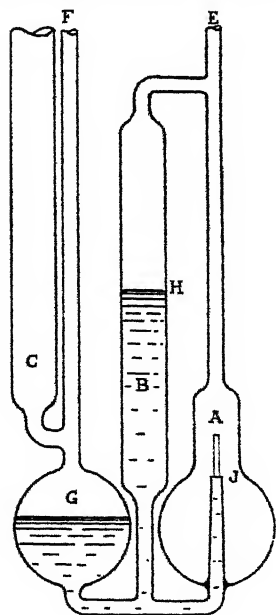


Fig. 1.

sealed to the tube J by means of a cement consisting of zinc oxide and sodium silicate. B is a tube about 1 cm. in diameter into which a head of molten metal was raised. G is a reservoir for the metal and C, a tube for introducing a cast rod of the solid metal. E and F were sealed to different parts of a rather elaborate system providing for the independent and accurate control of the pressure of the hydrogen. It is necessary that the capillary be circular, have a sharp edge and that the edge be perpendicular to the axis. These conditions were obtained by selection from many hundreds of short sections cut from finely drawn tubes. Sharp edges and ends perpendicular to the axes of the capillaries were obtained by scratching the capillaries with a razor blade and breaking. The ends were ascertained to be perpendicular by examination under a microscope. The diameters of the capillaries were measured with a calibrated comparator. The capillaries were not exactly circular in cross section, but the ellipticity was, in all cases, very small. The mean radii and the respective percentage differences between the major and minor axes were as follows: 0.02127, 0.94%; 0.02574, 0.58%; 0.01814, 0.55%; 0.02125, 0.65%.

Expansion of the quartz with the temperature was a negligible factor. The apparatus was heated by means

<sup>5</sup> Robt. Feustel, *Ann. phys.*, [4] 16, 61 (1905).



accuracy of temperature control is unnecessary, since the simultaneous decrease in surface tension and density means that the head of liquid metal necessary to force a drop out of the capillary varies but slowly with temperature.

### Experimental Procedure.

Before each determination it was necessary to heat the apparatus at  $500^{\circ}$  for a few hours while being evacuated to remove the adsorbed water vapor. At first this adsorbed water gave considerable trouble, especially at temperatures over  $450^{\circ}$ , but this was finally overcome by the preliminary heating.

When the apparatus had again cooled, a cast rod of the metal was introduced into the tube C which was again sealed. After repeatedly evacuating and washing out the whole line with hydrogen, the apparatus was again heated until the metal in C melted and ran into the reservoir G. Pressure was gradually applied at F, raising the metal into the column B. The change in level of the surface H was followed with a cathetometer, and its height was noted at the instant when drops of metal began to flow out of the top of A. The difference in head between the tip of the capillary and the surface H, multiplied by the density of the metal, gives the maximum pressure necessary to force a drop out of the tip. Shaking of the building caused a premature breaking of the drop so it was necessary to work during the quieter hours of the day.

In some of the determinations there was a slight capillary depression of the metal in the tube B. The magnitude of this depression was determined at the same time as the densities by a method described below. All determinations, with the exception of one with mercury, were made in an atmosphere of hydrogen at pressures somewhat greater than the vapor pressures of the metals.

### Density Determinations.

To calculate the surface tension it was necessary to know the densities of the metals at different temperatures. The densities were determined by measuring the difference in height of the metal in the two arms of a U-tube caused by a measured pressure difference.

The apparatus was designed to fit the furnace used in the surface tension work and is shown in Fig. 2.

D and H are tubes 3.5 cm. in diameter, large enough to have a negligible capillary depression; A, a long tube for inserting a rod of the metal, and C is a tube of the same diameter as B of Fig. 1. The tube C was inserted to determine the correction for capillary depression to be added to the observed heights in the surface tension determinations. E and F were sealed to the line constructed for controlling and measuring the pressure. The difference in pressure in E and F was measured by means of a manometer filled with sulfuric acid, the density of which was accurately determined. The difference in level of the metal in D and H was measured with a cathetometer.

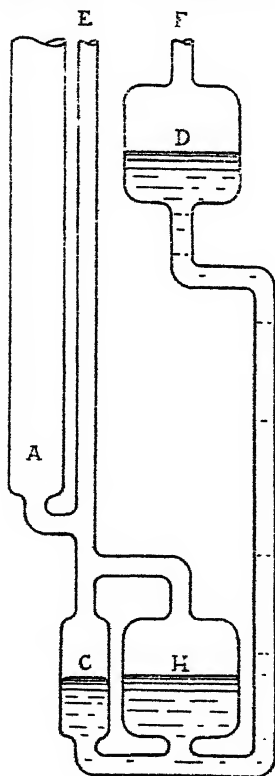


Fig. 2.

**Purification of Materials.**—Mercury was purified by washing and distilling c. p. mercury three times in accordance with methods recommended by Hulett.<sup>6</sup>

Bismuth was prepared by fusing twice reprecipitated bismuth oxychloride with pure potassium cyanide.

Electrolytic purification was used with the other metals, using anodes of as pure metal as was obtainable. The lead, tin and cadmium were pure commercial samples, the zinc from the Bertha mine of the New Jersey Zinc Company. The electrolytes were respectively lead perchlorate, stannic chloride, cadmium sulfate and zinc sulfate.

### Observations and Results.

**Densities.**—The following expressions represent the result of the density determinations. At least four temperatures were used with each substance. The maximum difference between the observed values and those calculated from the equations was 0.1%.

Zinc	$d = 6.59 - 0.00097(t - 419)$
Lead	$d = 10.71 - 0.00139(t - 327)$
Cadmium	$d = 8.02 - 0.00110(t - 320)$
Bismuth	$d = 10.07 - 0.00125(t - 269)$
Tin	$d = 7.01 - 0.00074(t - 232)$

**Surface Tensions.**—The data and the values of surface tensions calculated from the observations are given in Table I.

TABLE I.  
Observed Values of Surface Tension.

	$t$ ° C.	Press. H <sub>2</sub> mm.	No. of Observations.	Radius of capillary cm.	Aver. corrected height.	Density.	Surface tension, Dynes per cm.
Mercury	20	2.5	6	0.02127	3.30	13.54	465
	20	< 0.001	5	0.02127	3.30	13.54	465
	20	470	8	0.02127	3.30	13.54	465
		(air)					
	22	2	6	0.01814	3.83	13.54	461
	22	370	4	0.01814	3.83	13.54	461
	110	5	5	0.01814	3.77	13.33	447
	112	5	6	0.02127	3.28	13.33	454
	155	7	11	0.01814	3.75	13.22	441
	195	25	7	0.01814	3.73	13.13	434
	200	30	4	0.02127	3.20	13.12	436
	251	82	6	0.01814	3.64	12.99	421
	300	440	4	0.02127	3.03	12.87	405
	303	300	9	0.01814	3.57	12.87	408
	354	760	4	0.01814	3.47	12.76	394
Bismuth	320	3	4	0.02574	2.98	10.00	375
	365	3	6		2.97	9.95	371
	426	20	3		2.97	9.88	367
	472	20	5		2.96	9.82	365
Cadmium	339	100	7	0.02125	6.04	8.00	606
	366	145	7		6.16	7.97	616
	378	100	7		6.18	7.96	617

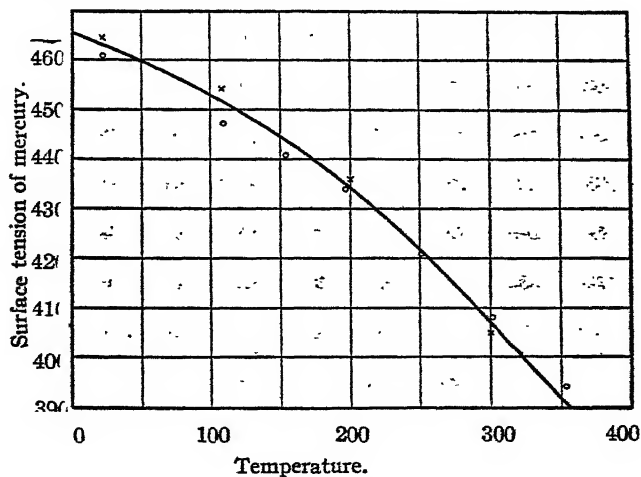
<sup>6</sup> G. A. Hulett, *Phys. Rev.*, **33**, 307 (1911).

TABLE I.—(Continued).

	$^{\circ}$ C.	Press. H <sub>2</sub> mm.	No. of Observations.	Radius of capillary cm.	Aver. corrected height.	Density.	Surface tension. Dynes per cm.
	421	100	3		6.26	7.92	622
	448	145	8		6.28	7.88	621
	508	100	3		6.29	7.82	619
	544	145	7		6.29	7.78	616
Lead	366	6	7	0.02574	3.30	10.65	442
	444	6	9		3.27	10.55	433
	522	6	5		3.27	10.44	429
Tin	362		5	0.01814	8.58	6.99	530
	319		6		8.46	6.95	519
	396		6		8.52	6.89	520
Zinc	477		5	0.02125	11.07	6.53	753
	543		9	0.02125	11.09	6.47	747

The maximum deviation from the averages here given was about 1% and in nearly all instances was very much less. The values for the surface tension of cadmium diminish with temperature below  $421^{\circ}$ , *i. e.*, the surface tension appears to go through a maximum. These values for cadmium were checked to within 1% by an independent determination using a different capillary but the duplicate set of values is not recorded in the table.

The values in Table I were plotted and the smooth curves drawn through the points are represented by the following equations. Only in the case of mercury does the range of temperature justify more than a linear equation. Fig. 3 gives the plot for mercury.



x-Values obtained with capillary of radius 0.02127 cm.

o-Values obtained with capillary of radius 0.01814 cm.

Fig. 3.

Mercury	$r = 467 - 0.043(t + 39) - 0.000386(t + 39)^2$
Bismuth	$r = 378 - 0.063(t - 269)$
Cadmium	$r = 630 - 0.065(t - 320)$
Lead	$r = 444 - 0.077(t - 327)$
Tin	$r = 531 - 0.080(t - 232)$
Zinc	$r = 758 - 0.090(t - 419)$

The first constant in the right hand member of each of the above equations represents the extrapolated values of the surface tension at the melting point. The equation for cadmium is determined only from the values at 421° and above.

Table II gives values of surface tension calculated at a series of temperatures from the smooth curves.

TABLE II.  
Surface Tensions.

Temp. ° C.	300	350	400	450	500
Bismuth.....	376	373	370	367	363
Lead.....	...	442	438	438	431
Tin.....	526	522	518	514	510
Cadmium.....	...	628	625	622	618
		(614 obs.)			
Zinc.....	...	...	...	755	751

Table III gives similar smoothed out values for mercury.

TABLE III.  
Surface Tension of Mercury.

Temp. ° C.....	0	20	50	100	150	200	250	300	350
Surface tension.....	465	463	460	453	445	435	422	408	393

### Discussion.

A comparison of the results obtained for the surface tensions in the present research with those obtained by previous observers is given in the following table.

TABLE IV.  
Comparison with Values by Other Observers.

	Temp. ° C.	Hogness. Cantor drop- pressure method.	Quincke. <sup>7</sup> Modified drop-weight method.	Siedentopf. <sup>8</sup> Dimensions of large drop.	Smith. <sup>9</sup> Capillary depression method.	Grundmach. <sup>10</sup> Ripple method.
Bismuth.....	269	378	465	429	346	...
Lead.....	327	444	537	509	425	482
Tin.....	232	531	681	612	480	352
Cadmium.....	320	630	815	830	...	...
Zinc.....	419	758	967(air) 1103(CO <sub>2</sub> )	...	707	...

<sup>7</sup> B. Quincke, *Pogg. Ann.*, 135, 642 (1868); 138, 141 (1869).

<sup>8</sup> Siedentopf, *Wied. Ann.*, 61, 235 (1897).

<sup>9</sup> S. W. Smith, *J. Inst. Metals*, 12, 168 (1914).

<sup>10</sup> Grundmach, *Ann. Phys.*, 3, 660 (1900).

Quincke used a modification of the drop-weight method which consisted in the melting of metal from a wire of known diameter. With mercury and tin, the usual drop weight was employed. The values given in the table have been corrected by the use of the formula of Lohnstein.<sup>11</sup> The correction is of doubtful accuracy, the experimental procedure was crude, and the metal surfaces undoubtedly contaminated by oxide so that the figures can hardly claim great weight.

The values by Siedentopf were calculated from the dimensions of a drop resting upon a flat surface in an atmosphere of carbon dioxide which would undoubtedly produce contamination of the surface with oxide, as is indicated by the high values.

Smith used the capillary depression method with a hole drilled in a piece of carbon. He made no correction for the angle of contact, which is certainly greater than zero, so that his low results are not surprising.

Grundmach measured the wave length of ripples upon the flat metallic surface, a method difficult to use with accuracy. He worked in an atmosphere of air which undoubtedly vitiates his figures for tin.

The surface tension of mercury has been determined by almost all of the known methods, and the values vary from 340 to 575 dynes per centimeter. The different determinations have been made *in vacuo* and in various gases. Quincke<sup>12</sup> has given a summary of all the earlier work with mercury.

More recently, Cenac,<sup>13</sup> using the drop-weight method, with two different correction terms, Lohnstein's and Rayleigh's, has given the following values for mercury:

	0° C. (air).	(Vacuum.).	100° (vac.).	180° (vac.).
Lohnstein.....	437	460	437	419
Rayleigh.....	445	467	443	425

The values *in vacuo* at 0°, agree well with ours, but at higher temperatures the values fall off somewhat more rapidly. Cantor using the method employed in this research obtained 459 dynes at 20° in air, and using the inverse procedure of blowing a bubble of air from a capillary immersed in the mercury obtained 466 dynes at 20° in air. Richards and Boyer,<sup>14</sup> by measuring the dimensions of a drop, found 441 dynes in air, a value considerably lower than ours. Harkins and Ewing,<sup>15</sup> using the drop weight method, give 476 dynes *in vacuo*, and Harkins and Grafton<sup>16</sup> 465 dynes in air.

<sup>11</sup> Lohnstein, *Ann. phys.*, 20, 237 (1906).

<sup>12</sup> Quincke, *Ann. phys.*, 61, 267 (1897).

<sup>13</sup> Cenac, *Ann. chim. phys.*, 28, 298 (1913).

<sup>14</sup> T. W. Richards and S. Boyer, *THIS JOURNAL*, 43, 274 (1921).

<sup>15</sup> Harkins and Ewing, *ibid.*, 42, 2539 (1920).

<sup>16</sup> Harkins and Grafton, *ibid.*, 42, 2534 (1920).

Since some observers claim lower results in air than *in vacuo*, it might be questioned whether the hydrogen present in the apparatus may not have somewhat altered the values. This point was tested by varying the pressure of hydrogen from 300 mm. down to a vacuum giving the green fluorescence of the glass with the electric discharge. The hydrogen was also replaced by an atmosphere of dry air. No detectable difference in the surface tension was found. In view of the large overvoltage of hydrogen on mercury, it would hardly be expected that it could be appreciably adsorbed. It was found, however, that, for some unknown reason, the first readings of these determinations gave low values. These values gradually increased as the determination proceeded and finally reached a limit for which the readings were very constant and concordant. It was also found that, unless all water vapor was removed from the apparatus and mercury by previous heating, results 3 or 4% too low, were obtained.

It should be pointed out that the method here employed avoids the large and somewhat uncertain correction for the diameter of the capillary necessitated by the drop-weight method. The correction factor in the drop-weight method, the  $f(r/a)$  developed by Lohnstein<sup>11</sup> and the  $f(r/V^{1/3})$  used by Harkins<sup>17</sup> is often as small as 0.6 and does not approach the limiting value of unity, while in the Cantor method, the correction term deviates only very slightly from this limiting value. In the present research for all the capillaries used, the correction factor

$$\left( 1 - \frac{2}{3} \frac{da}{p} - \frac{d^2 a^2}{p^2} \right)$$

was greater than 0.99.

### Summary.

The densities of liquid zinc, cadmium, tin, lead and bismuth have been determined at various temperatures.

The surface tension of mercury, cadmium, zinc, lead, tin and bismuth have been determined by the Cantor method of drop pressure.

It has been shown that there is no appreciable difference in the surface tensions of mercury in dry air, hydrogen and *in vacuo*.

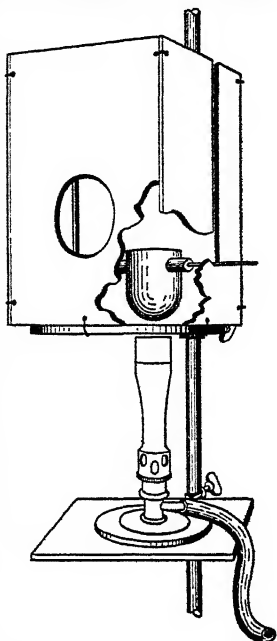
In conclusion the writer wishes to express his sincere appreciation to Professor J. H. Hildebrand, under whose direction the present work was carried on.

BERKELEY, CALIF.

<sup>17</sup> W. D. Harkins and F. E. Brown, *THIS JOURNAL*, 41, 499 (1919).

## NOTES.

**A New Type of Sodium Lamp for Polarimetry.**—To those persons who make use of a polariscope in their work the need of a constant and intense source of sodium light is one that is greatly felt. In this respect the authors believe that they have made a decided improvement by devising a simple arrangement which has served their purpose most admirably. Instead of any modification of the schemes used heretofore<sup>1</sup> they employ an alundum thimble or crucible as a reservoir for the salt which should preferably be sodium chloride. The thimble is exposed to the flame and as a result the sodium chloride melts, flows through the pores of the thimble and is vaporized in the flame so as to give a very intense illumination. The supply of material is large enough to insure a continuous source of light over a period of observation even to the extent of 5 or 6 hours if necessary. It is to be remarked, however, that in using this flame as with other sodium flames it is necessary for very precise work to use a dichromate light filter.



The general arrangement is portrayed in the accompanying sketch; while the details are discussed in the text under the three captions of shade, thimble and burner.

**Shade.**—The shade of the lamp is constructed of hard asbestos boarding about 3 to 4 mm. in thickness, the sides being bound by nickel or nickel-chromium wire passing through holes bored for this purpose. This shade is 14 cm. in height and 7.5 cm. square. A hole 3 cm. in diameter and 3.5 cm. from the bottom is cut in front, and constitutes the window for the light. On each side of the shade, 2.5 cm. from the back and extending to within 3.5 cm. from the bottom, are cut slits which allow the wire and suspended thimble to be lifted up and down, or removed and replaced at will. The whole shade is fastened at its bottom edge by wires to an iron ring which is movable up or down on a ring stand. This arrangement allows the adjustment of the shade with respect to the optical axis of the polariscope.

**Thimble.**—The alundum thimble should have a medium porosity; if the pores are too fine the molten sodium chloride filters through the thimble so slowly that the rate of vaporization is not enough to give proper intensity to the light; if the pores are too large the molten salt filters through the alundum more rapidly than it is vaporized and drops on the burner below. The thimble is suspended primarily by means of a silica tube which passes over a stout nickel or nickel-chromium wire.<sup>2</sup> The tube not only

<sup>1</sup> For a description of the various types of sodium light sources the reader is referred to Landolt, "Optical Rotation of Organic Substances," 1898, pp. 393-399. Browne, "Handbook of Sugar Analysis," 1912, pp. 147-149. Bur. Standards, *Bull.* No. 44 (Polarimetry), pp. 14-15 and 30-33 (1918).

<sup>2</sup> The silica tube can be obtained from a triangle made of this type of tubing.

protects the salt from contamination by the wire, but also protects the wire from the heat of the flame, thus preventing sagging. The holes in the alundum thimble, through which the silica tube passes, are easily and quickly bored with a rat-tail file or other sharp instrument, while the thimble itself can be cut down quickly to any size by means of a triangular file. The height of the thimble should be such that its top is in the same horizontal plane as the bottom of the window in the shade.

**Burner.**—The burner, which should preferably be of the Meker type, rests upon a movable platform attached to the same ring stand as the shade. The burner should be placed in such a position with respect to the thimble that the flame is not distorted by too close proximity, and so that the rear portion of the flame encounters the front part of the thimble.

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NEW YORK, N. Y. (Contribution No. 358)  
Received May 10, 1921.

**The Thermal Ionization of Metallic Vapors.**<sup>1</sup>—In a preceding paper,<sup>2</sup> the author has shown that the entropy of electron gas may be calculated from the same theoretical equation as for the other monatomic gases, namely,

$$S = \frac{5}{2} R \ln T - R \ln p + \frac{3}{2} R \ln M + S_1$$

where  $M$  is the molecular weight of the monatomic gas and  $S_1$  has the same value for all monatomic gases. Taking  $p$  in atmospheres,  $S_1$  has the value  $-3.2$  calories per degree.

This new theoretical knowledge may be used in predicting the thermal ionization of metallic vapors, a matter of some interest from the point of view of physical chemistry and astronomy.

**Derivation of Free Energy Equation for Ionization.**—Consider a metallic vapor which can dissociate into a positive ion and an electron in accordance with the reaction,



For the heat of the reaction of constant pressure and at temperature  $T$  we may evidently write,

$$\Delta H = EF + \frac{5}{2} RT \quad (2)$$

where  $E$  is the ionization potential of the metal in question,  $F$  is the value of the faraday,  $EF$  being the increase in the heat content of the system at the absolute zero, and  $\frac{5}{2} R T$  the value of  $\Delta C_p T$ .

For the change in the entropy of the system when the reaction occurs at constant temperature and under the standard conditions of unit partial pressure for each of the three components, we may obviously write from Equation 1,

$$\Delta S = \frac{5}{2} R \ln T + \frac{3}{2} R \ln M_E + S_1 \quad (3)$$

<sup>1</sup> Published by permission of the Chief of Ordnance.

<sup>2</sup> Tolman, *THIS JOURNAL*, **43**, 1592 (1921).



where  $M_{\pm}$  is the molecular weight of electron gas and we have neglected the slight difference between the molecular weights of the un-ionized vapor and its positive ion.<sup>3</sup>

We have thus obtained simple expressions (2) and (3) for the heat change and entropy change accompanying the reaction in which we are interested. We have, however, the following fundamental equation of definition connecting free energy with heat content and entropy, namely,

$$\Delta F = \Delta H - T \Delta S \quad (4)$$

Introducing (2) and (3) we obtain,

$$\Delta F = EF - \frac{5}{2} R T \ln T + \left( \frac{5}{2} R - \frac{3}{2} R \ln M_{\pm} - S_1 \right) T. \quad (5)$$

It is interesting to note that this equation has the same form as that of the familiar free energy equation,

$$\Delta F = \Delta H_0 - \Delta C_p T \ln T + I T$$

and the corresponding quantities have precisely the same significance.

**Calculation of Ionization Constant.**—In order to determine the degree of ionization of the vapor we may substitute Equation 5 into the well-known expression connecting free energy change with equilibrium constant,

$$\Delta F = -R T \ln K_p = -R T \ln \frac{p_{R^+} p_{E^-}}{p_R}. \quad (6)$$

We obtain,

$$\ln K_p = -\frac{EF}{RT} + \frac{5}{2} \ln T - \left( \frac{5}{2} - \frac{3}{2} \ln M_{\pm} - \frac{S_1}{R} \right). \quad (7)$$

If  $K_p$  is the equilibrium constant using partial pressures expressed in atmospheres,  $E$  is the ionization potential in volts,  $T$  is in degrees Kelvin, and we change to common logarithms and use the values  $F = 96540$  coulombs,  $M_{\pm} = 5.44 \times 10^{-4}$  grams,  $S = -3.2$  calories per degree and  $R = 1.985$  calories per degree we obtain,

$$\log K_p = -\frac{5040 E}{T} + 2.5 \log T - 6.69. \quad (8)$$

**Ionization of Calcium Vapor in the Sun's Atmosphere.**—The use of this equation in predicting the degree of ionization of metallic vapors in the electric arc or the atmosphere of the sun will be obvious.

For example, if we take the ionization potential of calcium vapor as 6.1 volts, the partial pressure of un-ionized calcium vapor in the sun's

<sup>3</sup> Equation 3 involves the assumption that we are justified in considering all three gases  $R$ ,  $R^+$  and  $E^-$  as monatomic even at the high temperatures involved. It is of course possible that the atoms of the metallic vapor would pick up rotational energy at high temperatures and hence that their entropy should be calculated from the formula for a diatomic or polyatomic gas.

atmosphere as 4 atmospheres, and the temperature as  $5500^{\circ}$  absolute, the partial pressure of calcium ion or of electron gas comes out 0.07 atmospheres corresponding to 1.7% ionization. This means that the sun's atmosphere has a very considerable electrical conductivity which can be calculated by making proper estimates of the ionic mobilities.

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**Addendum.**—In connection with my recent article on "The Ionization of Aqueous Solutions of Ammonia in the Presence of Urea," published in the December, 1920, number of *THIS JOURNAL*, the following addendum should be made.

"This paper embodies the subject matter of a thesis presented to the Faculty of Clark University in partial fulfilment of the requirements for the Degree of Master of Arts. I wish to acknowledge my indebtedness to the Chemical Laboratory of Clark University for the use of the facilities of this Laboratory in connection with this investigation, and to Dr. Kraus for his interest and coöperation which made this investigation possible."

TOOELE, UTAH.  
Received January 11, 1921.

WINTHROP M. BURKE.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

## AROMATIC ARSENIC COMPOUNDS. IX. DIAZO-AMINO COMPOUNDS OF ARSANILIC ACID AND ITS DERIVATIVES.

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

Received June 29, 1920.

In a former communication<sup>1</sup> there was outlined a plan for the synthesis of aromatic arsenic compounds for chemotherapeutic study in which, among other series of substances which have since been published, were mentioned the two groups of diazo-amino and azo derivatives obtained from arsanilic acid. These substances with the first which we prepared for these investigations, and although interesting results were obtained with individual compounds in the treatment of experimental trypanosomiasis, we were soon led to discontinue the study of these types because of disadvantages which seemed inherent in them, such as the general instability of the diazo-amino compounds and certain harmful toxic effects induced by both groups. We believe, however, that a presentation of our chemical studies with these compounds should not be devoid of interest.

<sup>1</sup> *THIS JOURNAL*, 41, 1581 (1919).

In their determination of the constitution of arsanilic acid Ehrlich and Bertheim<sup>2</sup> found that the amino group could be readily diazotized and that the resulting diazo compound coupled without difficulty, yielding azo dyes. We have found that this reaction could be extended to the preparation of well-defined diazo-amino compounds containing the arsonic acid residue. We have prepared several groups of such substances, using as couplers dialkylamines, simple arylamines, aminobenzoic acids, arylglycines, and amino-phenoxyacetic acids.

The coupling of the secondary aliphatic amines and the simpler primary aromatic amines with diazotized arsanilic acid offered as a rule but little difficulty, the procedure being that adopted in the past for analogous substances. The reaction mixture was kept neutral or acid only with a weak acid such as acetic acid. The isolation of the individual compounds was accomplished either as the salt or as the acid, depending upon manipulative convenience. In certain cases it was found preferable, however, to diazotize the amino compound first and then to add arsanilic acid as the coupler. In the case of the aromatic amino acids, although coupling usually proceeded smoothly, it required considerable experimentation to determine in what form and under what conditions the product could best be isolated, since there were available the free acid, the monosodium salt, and the disodium salt from which to choose. The simpler aminobenzoic acids yielded diazo compounds under carefully controlled conditions by using the amino acid itself as coupler and isolating the products as the monosodium salts. In the first experiments in which *p*-amino-phenoxyacetic acid and its homologs were employed, however, it developed that the reaction either did not proceed entirely in the desired sense, or that the diazo-amino compounds possessed properties which rendered difficult their isolation from the reaction mixture. In such cases it was found that the amino acid esters coupled smoothly, giving the diazo-amino esters in excellent yield. Owing to the stability of the diazo-amino group on the alkaline side it then proved relatively simple to saponify the esters to the diazo-amino acids themselves. This method was consequently employed as a more certain means of obtaining these acids in satisfactory form and yield from the more complex amino-aryl acids, although in some instances the direct method might have been employed. This device also proved necessary in the preparation of the diazo-amino compound from *p*-aminophenol. Here *p*-aminophenyl benzoate was diazotized and coupled with arsanilic acid, yielding the diazo-amino benzoate, which was subsequently saponified.

The diazo-amino compounds derived from the secondary aliphatic amines and from most of the aromatic amino compounds formed both crystalline acids and sodium salts, the former possessing definite decompo-

<sup>2</sup> Ehrlich and Bertheim, *Ber.*, 40, 3292 (1907).

sition points and being as a rule difficultly soluble in the usual solvents, while the salts formed more or less yellow solutions in water. The acids were unstable in acid solution, readily dissociating into the component amino and diazo compounds and evolving nitrogen on warming. In the case of several of the diazo-amino compounds derived from the arylglycines and the methyl derivatives of *p*-amino-phenoxyacetic acid, it was found impossible to isolate the free acids owing to their slight tendency to crystallize and to the ease with which they dissociated in acid solution. On the other hand, the esters of these substances, with few exceptions, proved to be more stable and easy to isolate. Practically all of the diazo-amino sodium salts were readily soluble in water, the solutions giving immediate precipitates with the heavy metal ions.

On the whole the work with this class of substances proved difficult, since in each case the conditions best suited for the preparation and isolation of the particular compound had to be carefully studied. It was also found essential to work as rapidly as possible throughout, and at low temperatures in order to avoid the decomposition which otherwise readily occurred.

Owing to the mass of detail the work is presented practically in abstract form, in order not to use undue space.

### Experimental.

The values given for water of crystallization were obtained with substances which had been dried to constant weight in the air. Water was determined as a rule by drying *in vacuo* at room temperature over sulfuric acid, since higher temperatures caused decomposition.

In order to avoid repetition, it will be understood that the diazotization of arsanilic acid was carried out as follows. Arsanilic acid was dissolved in 2 molecular equivalents of *N* hydrochloric acid, chilled to about 5° and diazotized with one equivalent of 5 *N* sodium nitrite solution. The reaction proceeded smoothly and completely and toward the end there was a pronounced color change from orange to pale yellow. The solution was then neutralized before coupling according to the method given under each compound to be described. The expression  $A \rightarrow B$  indicates that the diazotized arsanilic acid solution was added to the coupler;  $B \rightarrow A$ , that the coupler was added to the diazotized arsanilic acid.

In cases in which no acid group was present in addition to the arsonic acid residue, acetic acid was in all cases sufficient to liberate the diazo-amino arsonic acid from solutions of the sodium salt. It was also found advantageous to work at rather high dilutions, except in the case of the aliphatic amines. When an additional carboxy group was present it was found necessary to add to the chilled solutions of the salt sufficient hydrochloric acid to render the reaction just acid to congo red.

## (A) Diazo-amino Compounds of Arsanilic Acid and Aliphatic Amines.

**Diazobenzene - (4-arsonic acid) - dimethylamine.**—B  $\longrightarrow$  neutralized A, coupling being complete in about 15 minutes. After adding acetic acid the product was recrystallized from alcohol, forming orange spears which intumesced at 182°. It is very difficultly soluble in cold alcohol, more readily in methyl alcohol, and decomposes in boiling water with nitrogen evolution.

*Analyses.* Calc. for  $C_8H_{12}O_3N_3As$ : N, 15.38; As, 27.44. Found: N, 15.52; As, 27.13.

On treating an alcoholic suspension with 1 mol. of 25% sodium hydroxide solution, heating, and carefully adding water until clear, the sodium salt crystallized on cooling, separating from 85% alcohol as glistening, salmon-colored platelets which dissolve easily in water.

*Analyses.* Calc. for  $C_8H_{11}O_3N_3AsNa \cdot 3.5H_2O$ :  $H_2O$ , 17.60. Found: 17.89.

Calc. for  $C_8H_{11}O_3N_3AsNa$ : N, 14.24. Found: 14.42.

**Diazobenzene - (4-arsonic acid) - diethylamine.**—The crude acid was reprecipitated from dil. sodium carbonate, dissolved in warm 50% alcohol, and cautiously diluted with an equal volume of water, separating as delicate, flat, cream-colored needles, which, when anhydrous, gradually soften and darken above 120°, decompose at about 195–200°, and dissolve readily in methyl alcohol and acetic acid.

*Analyses.* Calc. for  $C_{10}H_{16}O_3N_3As \cdot H_2O$ :  $H_2O$ , 5.65. Found: 6.51.

Calc. for  $C_{10}H_{16}O_3N_3As$ : N, 13.96; As, 24.88. Found: N, 13.59; As, 25.12.

A neutral aqueous solution of the sodium salt was prepared, evaporated to dryness *in vacuo*, and the residue dissolved in a little hot 85% alcohol, the salt slowly crystallizing in the cold as rosetts of somewhat deliquescent cream-colored needles.

*Analyses.* Calc. for  $C_{10}H_{16}O_3N_3AsNa$ : N, 13.00; As, 23.21. Found: N, 13.02; As, 23.82.

**Diazobenzene - (4-arsonic acid) - piperidine.**—The free acid, obtained from its salt, formed pale drab spherules and rosetts of narrow, microscopic platelets which melt and effervesce at 162–3°, and are appreciably soluble in methyl and ethyl alcohol.

*Analyses.* Calc. for  $C_{11}H_{16}O_3N_3As$ : N, 13.42; As, 23.93. Found: N, 13.53; As, 23.69.

Separation of the sodium salt from the initial reaction mixture was facilitated by the addition of sodium acetate. It forms drab-colored, minute platelets from 85% alcohol.

*Analyses.* Calc. for  $C_{11}H_{16}O_3N_3AsNa \cdot 3.5H_2O$ :  $H_2O$ , 15.83. Found: 15.35.

Calc. for  $C_{11}H_{16}O_3N_3AsNa$ : N, 12.53. Found: 12.57.

**Bis-diazobenzene - (4-arsonic acid) - pentamethylene-tetramine.**—8.7 g. of arsanilic acid were diazotized with 40 cc. of *N* sodium nitrite solution, diluted with an equal volume of saturated sodium acetate solution, and then treated with 3 g. of hexamethylene-tetramine.<sup>3</sup> Coupling occurred rapidly with cleavage of formaldehyde, and 8 g. of the sodium salt quickly crystallized. Rapid recrystallization from water yielded lustrous, colorless platelets soluble in about 20 parts of water at ordinary temperatures.

*Analyses.* Calc. for  $C_{17}H_{20}O_6N_8As_2Na_2 \cdot 6H_2O$ :  $H_2O$ , 14.68. Found: 14.31.

Calc. for  $C_{17}H_{20}O_6N_8As_2Na_2$ : N, 17.83. Found: 17.65.

On slowly treating a very dilute solution in warm water with acetic acid the free acid separates as narrow, minute, colorless, microscopic platelets which are practically insoluble in neutral solvents. It puffs up at 210–12°, and dissolves very slowly in boiling water with nitrogen evolution, decomposition occurring rapidly on addition of a drop of acid, when the odor of formaldehyde becomes quite noticeable.

*Analyses.* Calc. for  $C_{17}H_{20}O_6N_8As_2$ : N, 19.18; As, 25.66. Found: N, 19.15; As, 25.40.

<sup>3</sup> Cf. Duden and Scharf, *Ann.*, 288, 218 (1895).

## (B) Diazo-amino Compounds of Arsanilic Acid and the Simpler Aromatic Amines.

**Diazobenzene - 4-(arsonic acid) - aniline.**—Alcoholic B  $\longrightarrow$  neutralized A. The yellow sodium salt gradually crystallized on adding sodium acetate, separating from 85% alcohol as minute, orange platelets and flat needles which dissolve readily in water.

*Analyses.* Calc. for  $C_{12}H_{11}O_3N_3AsNa \cdot 4H_2O$ :  $H_2O$ , 17.35. Found: 17.02.

Calc. for  $C_{12}H_{11}O_3N_3AsNa$ : N, 12.24. Found: 12.21.

The free acid forms bundles of minute, yellow, microscopic needles which melt and then decompose at 112–13°. It is difficultly soluble in cold methyl and ethyl alcohols but quite readily on boiling, and decomposes in boiling water.

*Analyses.* Calc. for  $C_{12}H_{12}O_3N_3As$ : N, 13.08; As, 23.33. Found: N, 12.77; As, 23.55.

**Diazobenzene - (4-arsonic acid) - methylaniline.**—Alcoholic B  $\longrightarrow$  A + sodium acetate yielded a brown, gummy precipitate which crystallized on rubbing. On dissolving in very dilute aqueous ammonia, adding an equal volume of alcohol, cooling, and acidifying with acetic acid, the pure acid separated as orange-brown aggregates of minute radiating needles, effervescing at 160–2° with preliminary reddening. It dissolves in dil. acid with an orange-red color appearing a faint purple in thin layers, apparently due to partial dye formation, although the solution still evolves nitrogen on heating.

*Analyses.* Calc. for  $C_{13}H_{14}O_3N_3As$ : N, 12.54. Found: 12.58.

When the diazo solution was neutralized with sodium hydroxide and then coupled with methylaniline, a deep brown-orange solution resulted from which the sodium salt separated on adding sodium acetate, as a thick paste of lustrous, orange platelets which were recrystallized from water.

*Analyses.* Calc. for  $C_{12}H_{13}O_3N_3AsNa \cdot 5.5H_2O$ :  $H_2O$ , 21.70. Found: 21.53.

Calc. for  $C_{13}H_{13}O_3N_3AsNa$ : N, 11.76; As, 21.00. Found: N, 11.83; As, 21.30.

**Diazobenzene - (4-arsonic acid) - p - toluidine.**—The sparingly soluble sodium salt separated in almost quantitative yield, forming yellow, glistening leaflets from water containing a few drops of dil. sodium carbonate.

*Analyses.* Calc. for  $C_{13}H_{13}O_3N_3AsNa \cdot 6H_2O$ :  $H_2O$ , 23.23. Found: 22.79.

Calc. for  $C_{13}H_{13}O_3N_3AsNa$ : N, 11.76; As, 20.99. Found: N, 11.78; As, 20.79.

The free acid is precipitated from a 50% alcoholic solution of the salt as thin, pale yellow, microscopic needles which intumesce at 130–2° and dissolve in hot alcohol.

*Analysis.* Calc. for  $C_{13}H_{14}O_3N_3As$ : N, 12.53. Found: 12.63.

**Diazobenzene - (4-arsonic acid) - 4' - chloro-aniline.**—B + dil. hydrochloric acid  $\longrightarrow$  A + sodium acetate. The acid immediately precipitated in quantitative yield and gradually crystallized. Dissolved in much 50% alcohol with the aid of sodium hydroxide and re-acidified it forms an emulsion which rapidly changes on rubbing to hexagonal platelets which intumesce at 177° with preliminary darkening and are practically insoluble in neutral solvents.

*Analysis.* Calc. for  $C_{12}H_{11}O_3N_3ClAs$ : N, 11.82. Found: 12.08.

Dissolved in 1 mol. of dil. sodium hydroxide solution it yielded the sodium salt on addition of alcohol, forming almost colorless platelets from 50% alcohol.

*Analyses.* Calc. for  $C_{12}H_{10}O_3N_3ClAsNa \cdot 2H_2O$ :  $H_2O$ , 8.71. Found: 8.37.

Calc. for  $C_{12}H_{10}O_3N_3ClAsNa$ : N, 11.12; As, 19.86. Found: N, 11.20; As, 20.01.

**Diazobenzene - (4-arsonic acid) - o - anisidine.**—Although Jacobson and Hönigsberger<sup>4</sup> obtained a dye in using o-anisidine as a coupler, the method used in the above cases yielded the diazo-amino derivative. A certain amount of dye formation was, however, evident from the deep color. The sodium salt was salted out with sodium

<sup>4</sup> Jacobson and Hönigsberger, *Ber.*, 36, 4096 (1903).

acetate and washed with alcohol. It separates from 85% alcohol as aggregates of brown, rectangular platelets dissolving readily in water.

*Analyses.* Calc. for  $C_{13}H_{13}O_4N_3AsNa \cdot 5H_2O$ :  $H_2O$ , 19.44. Found: 20.02.

Calc. for  $C_{13}H_{13}O_4N_3AsNa$ : N, 11.26. Found: 11.19.

The free acid was precipitated from a chilled solution of the salt in 50% alcohol as sheaves of flat, microscopic needles which, when anhydrous, sinter, then darken, and finally intumesce at 95–9°.

*Analyses.* Calc. for  $C_{13}H_{14}O_4N_3As \cdot 2.5H_2O$ :  $H_2O$ , 11.37. Found: 10.58.

Calc. for  $C_{13}H_{14}O_4N_3As$ : N, 11.97. Found: 12.10.

**Diazobenzene - (4-arsonic acid) - *p* - anisidine.**—The sodium salt separates from 50 % alcohol as rosetts of pale brown leaflets.

*Analyses.* Calc. for  $C_{13}H_{13}O_4N_3AsNa \cdot 5H_2O$ :  $H_2O$ , 19.44. Found: 19.55.

Calc. for  $C_{13}H_{13}O_4N_3AsNa$ : N, 11.26; As, 20.08. Found: N, 11.39; As, 20.01.

The free acid was precipitated from a 33% alcoholic solution of the salt as pale brown aggregates of microscopic leaflets which sinter and begin to decompose at about 110° and intumesce slowly at 116–9° when anhydrous, and are quite soluble in methyl alcohol.

*Analyses.* Calc. for  $C_{13}H_{14}O_4N_3As \cdot 0.5H_2O$ :  $H_2O$ , 2.50. Found: 2.36.

Calc. for  $C_{13}H_{14}O_4N_3As$ : N, 11.97. Found: 11.88.

**Diazobenzene - (4-arsonic acid) - 4' - amino-acetanilide.**—The sodium salt separated from 50% alcohol as plumes of tan, microscopic leaflets.

*Analyses.* Calc. for  $C_{14}H_{14}O_4N_4AsNa \cdot 5H_2O$ :  $H_2O$ , 18.36. Found: 17.38.

Calc. for  $C_{14}H_{14}O_4N_4AsNa$ : N, 14.00; As, 18.74; Found: N, 13.88; As, 18.49.

The free acid liberated from the salt in 50% alcohol forms long, drab, lustrous hexagonal, microscopic platelets, which decompose at 165–70° when anhydrous.

*Analyses.* Calc. for  $C_{14}H_{15}O_4N_4As \cdot H_2O$ :  $H_2O$ , 4.54. Found: 4.80.

Calc. for  $C_{14}H_{15}O_4N_4As$ : N, 14.81. Found: 14.79.

**Diazobenzene - (4-arsonic acid) - 4' - aminophenyl benzoate.**—6.4 g. of well powdered *p*-aminophenyl benzoate<sup>5</sup> suspended in 60 cc. of *N* hydrochloric acid were slowly diazotized at 10° with 2.2 g. of sodium nitrite. After 15 minutes' additional turbing the solution was filtered from a small amount of undissolved material and then treated, with stirring, with 6.6 g. of arsanilic acid in 30 cc. of *N* sodium hydroxide solution. The light yellow, pasty diazo-amino compound solidified completely on standing overnight in the ice-box. The yield was 12 g. A portion, dissolved in a large volume of warm methyl alcohol and cautiously treated with water until crystallization began on rubbing, formed thin, yellow, microscopic leaflets which decompose at 155–8° and are practically insoluble in neutral solvents except hot methyl and ethyl alcohols.

*Analysis.* Calc. for  $C_{19}H_{19}O_6N_3As$ : N, 9.52. Found: 9.65.

**Diazobenzene - (4-arsonic acid) - 4' - aminophenol.**—The crude benzoate was dissolved in 4 equivalents of 2 *N* sodium hydroxide solution, allowed to stand for 15 minutes at room temperature, saturated with sodium acetate, and then chilled and neutralized with acetic acid. On rubbing the sodium salt slowly crystallized, separating from 85% alcohol as rosetts of yellow microscopic needles. Under carefully controlled conditions acetic acid precipitated the microcrystalline acid which, however, was too unstable to isolate.

*Analyses.* Calc. for  $C_{12}H_{11}O_4N_3AsNa \cdot 4H_2O$ :  $H_2O$ , 16.69. Found: 16.38.

Calc. for  $C_{12}H_{11}O_4N_3AsNa$ : N, 11.69; As, 20.87. Found: N, 11.34; As, 20.76.

**Diazobenzene - (4-arsonic acid) - 4' - amino-acetophenone.**—A + 1 mol. alkali → diazotized B + sodium acetate. The resulting sodium salt, recrystallized from 85% alcohol, formed brownish-yellow rosetts of minute, flat needles.

*Analyses.* Calc. for  $C_{14}H_{13}O_4N_3AsNa \cdot 6H_2O$ :  $H_2O$ , 21.91. Found: 21.51.

<sup>5</sup> Cf. Wohl, *Ber.*, 36, 4143 (1903).

Calc. for  $C_{14}H_{13}O_4N_3AsNa$ : N, 10.91. Found: 10.94.

The free acid consists of sheaves of bright yellow, microscopic needles which intumesce to a reddish mass at  $177-8^\circ$  after preliminary darkening and sintering, and dissolve in boiling methyl alcohol.

*Analyses.* Calc. for  $C_{14}H_{14}O_4N_3As$ : N, 11.57; As, 20.63. Found: N, 11.40; As, 20.91.

### (C) Diazo-amino Compounds of Arsanilic Acid and the Aminobenzoic Acids.

**Diazobenzene - (4-arsonic acid) - 2' - aminobenzoic acid.**—Only the following conditions were found to yield this substance and its salts in pure form. 8.7 g. of arsanilic acid diazotized in 80 cc. of *N* hydrochloric acid were treated with 80 cc. of saturated sodium acetate solution and then with 5.5 g. of anthranilic acid dissolved in 80 cc. of *N* sodium hydroxide solution. The monosodium salt soon separated in almost quantitative yield as a brownish-yellow powder. On dissolving in dil. sodium hydroxide solution, adding sodium acetate and then a slight excess of acetic acid, a gelatinous mass formed which rapidly changed to radiating masses of flat, yellow microscopic needles of the monosodium salt. The substance is difficultly soluble in cold water.

*Analyses.* Calc. for  $C_{13}H_{11}O_5N_3AsNa \cdot 4.5H_2O$ :  $H_2O$ , 17.31. Found: 16.74

Calc. for  $C_{13}H_{11}O_5N_3AsNa$ : N, 10.85. Found: 11.06.

A concentrated solution prepared with an additional mol. of sodium hydroxide yielded with sodium acetate the yellow disodium salt which crystallized from 85% alcohol as long, flat, yellow needles, dissolving easily in water with a yellow color.

*Analyses.* Calc. for  $C_{13}H_{10}O_5N_3AsNa_2 \cdot 8H_2O$ :  $H_2O$ , 26.05. Found: 26.37.

Calc. for  $C_{13}H_{10}O_5N_3AsNa_2$ : N, 10.26; As, 18.32. Found: N, 10.14; As, 17.

With a large excess of acetic acid, it immediately gives the free acid as thin, yellow, microscopic needles which intumesce at  $160^\circ$ , and dissolve in hot methyl or ethyl alcohol.

*Analysis.* Calc. for  $C_{13}H_{13}O_5N_3As$ : N, 11.51. Found: 11.51.

**Diazobenzene - (4-arsonic acid) - 3' - aminobenzoic acid.**—The same conditions were used, except that the addition of 12 cc. of 50% acetic acid was necessary to cause the precipitation of the monosodium salt. Recrystallized as in the preceding preparation it forms a cream-colored, microcrystalline, anhydrous salt.

*Analysis.* Calc. for  $C_{13}H_{11}O_5N_3AsNa$ : N, 10.85. Found: 10.71.

An aqueous suspension was dissolved with just sufficient sodium hydroxide and treated with absolute alcohol to incipient turbidity. The resulting disodium salt separated from 70% alcohol as long, thin, pale yellow, microscopic needles.

*Analyses.* Calc. for  $C_{13}H_{10}O_5N_3AsNa_2 \cdot 6.5H_2O$ :  $H_2O$ , 22.24. Found: 21.68.

Calc. for  $C_{13}H_{10}O_5N_3AsNa_2$ : N, 10.26. Found: 10.32.

A well chilled solution in 50 parts of 50% alcohol was made just acid to congo red, the arsonic acid then separating as buff-colored microcrystalline rosetts which intumesce at  $141^\circ$  and dissolve in hot methyl and ethyl alcohols.

*Analyses.* Calc. for  $C_{13}H_{13}O_5N_3As$ : N, 11.51; As, 20.52. Found: N, 11.29; As, 20.54.

**Diazobenzene - (4-arsonic acid) - 4' - aminobenzoic acid.**—The special conditions necessary were treatment of the well chilled diazotate from 4.4 g. of arsanilic acid in 40 cc. of *N* hydrochloric acid with 60 cc. of alcohol and then rapidly with a solution of 2.8 g. of *p*-aminobenzoic acid in 10 cc. of 2 *N* sodium hydroxide solution. The deep brown solution deposited the yellow, amorphous monosodium salt almost at once and this changed to aggregates of microscopic needles under 50% alcohol. It was dissolved in 50% alcohol with a little sodium hydroxide and again acidified with acetic acid in slight excess, crystallizing in anhydrous form on rubbing. It is very sparingly soluble in cold water. The free acid formed flat, microscopic needles, but was not obtained pur



*Analyses.* Calc. for  $C_{13}H_{11}O_6N_3AsNa$ : N, 10.85; As, 19.36. Found: N, 11.07; As, 19.23.

**Diazobenzene - (4-arsonic acid) - 3' - amino-6'-methoxybenzoic methyl ester.**—B hydrochloride  $\rightarrow$  A + sodium acetate. The resulting thick, gelatinous mass crystallized after adding one-half volume of alcohol and stirring and chilling. Dissolved in much cold alcohol and treated with an equal volume of water the ester acid crystallized as buff-colored aggregates of narrow platelets with notched ends, melting and evolving gas at 90–95° and dissolving readily in methyl or ethyl alcohol, especially on warming.

*Analyses.* Calc. for  $C_{16}H_{13}O_6N_3As \cdot 3H_2O$ :  $H_2O$ , 11.31. Found: 11.08.

Calc. for  $C_{16}H_{13}O_6N_3As$ : N, 9.93. Found: 10.18.

**Diazobenzene - (4-arsonic acid) - 3' - amino-6'-methoxybenzoic acid.**—The ester, warmed for one hour in 50% alcohol containing 3 mols. of sodium hydroxide, neutralizing with 1 mol. of acetic acid, and adding alcohol to incipient turbidity, gave the **disodium salt**, which separated from 70% alcohol as rosetts of pale, brownish-yellow, hygroscopic needles.

*Analysis.* Calc. for  $C_{14}H_{12}O_6N_3AsNa_2$ : N, 9.57. Found: 9.67.

The arsonic acid was precipitated in 50% alcohol as rosetts of yellow microscopic needles which decompose at 140° when anhydrous.

*Analyses.* Calc. for  $C_{14}H_{14}O_6N_3As \cdot 1.5H_2O$ :  $H_2O$ , 6.40. Found: 6.47.

Calc. for  $C_{14}H_{14}O_6N_3As$ : N, 10.63. Found: 10.64.

**Diazobenzene - (4-arsonic acid) - 3' - amino-anisic methyl ester.**—Alcoholic B  $\rightarrow$  A + sodium acetate. The ester acid, recrystallized from much 50% alcohol, forms glistening yellow needles which decompose at about 150° with preliminary darkening, and dissolve readily in methyl alcohol.

*Analyses.* Calc. for  $C_{16}H_{13}O_6N_3As \cdot 2.5H_2O$ :  $H_2O$ , 9.91. Found: 9.20.

Calc. for  $C_{16}H_{13}O_6N_3As$ : N, 10.26. Found: 10.37.

**Diazobenzene - (4-arsonic acid) - 3' - amino-anisic acid.**—I. Best prepared by saponification of the ester as described for the isomeric *o*-methoxy derivative. From 70% alcohol the disodium salt forms balls of fine yellow needles. II. The salt was also obtained directly, although in poorer yield, by the reaction of sodium 3-amino-anisate with the neutralized diazo solution and the addition of an equal volume of absolute alcohol.

*Analyses.* Calc. for  $C_{14}H_{12}O_6N_3AsNa_2 \cdot 10H_2O$ :  $H_2O$ , 29.08. Found: I, 30.13; II, 30.36.

Calc. for  $C_{14}H_{12}O_6N_3AsNa_2$ : N, 9.57; As, 17.08. Found: N, I, 9.68; II, 9.69; As, 17.23, 16.92.

The free acid was precipitated from 50% alcohol as aggregates of minute, yellow, microscopic needles which intumesce at 150–5° with preliminary darkening when anhydrous and are difficultly soluble in hot methyl alcohol.

*Analyses.* Calc. for  $C_{14}H_{14}O_6N_3As \cdot 1.5H_2O$ :  $H_2O$ , 6.40. Found: 6.30.

Calc. for  $C_{14}H_{14}O_6N_3As$ : N, 10.63. Found: 10.63.

**Diazobenzene - (4-arsonic acid) - 6' - aminopiperonylic methyl ester.**—B hydrochloride  $\rightarrow$  A, followed by sodium acetate. Reprecipitated from very dilute aqueous ammonia the ester acid forms minute aggregates of short, flat, almost colorless needles which do not decompose below 280° and are practically insoluble in the neutral solvents.

*Analysis.* Calc. for  $C_{16}H_{14}O_7N_3As$ : N, 9.92. Found: 9.91.

On saponification, a sodium salt was easily obtained, which, however, gave poor analytical figures, as did also the acid obtained from it. An attempt to prepare the diazo-amino acid directly from 6-aminopiperonylic acid yielded a dye which was not investigated further.

**Diazobenzene - (4-arsonic acid) - 4' - aminocinnamic ethyl ester.**—3.8 g. of amino ester were diazotized in 60 cc. of *N* hydrochloric acid with chilling and treated with 20 cc.

of *N* sodium hydroxide solution. Without filtering from the yellow precipitate which formed, 4.4 g. of arsanilic acid in 20 cc. of *N* sodium hydroxide solution were added and finally 50 cc. of saturated sodium acetate solution. The initial amorphous precipitate changed to flat, yellow, microscopic needles of the sodium salt, which separates from 70% alcohol as bright yellow microscopic needles which are sparingly soluble in cold water.

*Analyses.* Calc. for  $C_{17}H_{17}O_6N_3AsNa \cdot 6H_2O$ :  $H_2O$ , 19.67. Found: 19.69.

Calc. for  $C_{17}H_{17}O_6N_3AsNa$ : N, 9.52. Found: 10.08.

The arsonic acid forms aggregates of fine, yellow, microscopic needles which decompose at 155–60°.

*Analysis.* Calc. for  $C_{17}H_{15}O_6N_3As$ : N, 10.02; As, 17.89. Found: N, 10.32; As, 17.88.

**Diazobenzene - (4-arsonic acid) - 4' - aminocinnamic acid.**—The ester salt was saponified in 50% alcohol containing 2 mols. of sodium hydroxide, followed by 1 mol. of acetic acid, and then alcohol. Recrystallized from 70% alcohol the disodium salt formed yellow microscopic needles which dissolved readily in water.

*Analyses.* Calc. for  $C_{15}H_{12}O_6N_3AsNa_2 \cdot 6H_2O$ :  $H_2O$ , 19.89. Found: 19.96.

Calc. for  $C_{15}H_{12}O_6N_3AsNa_2$ : N, 9.66; As, 17.23. Found: N, 9.43; As, 16.83.

The acid is precipitated from 50% alcohol as a gelatinous mass which changes to yellow, microscopic needles which decompose at 155–60° with preliminary darkening and sintering when anhydrous, and are appreciably soluble in boiling methyl alcohol.

*Analyses.* Calc. for  $C_{15}H_{14}O_6N_3As \cdot 0.5 H_2O$ :  $H_2O$ , 2.25. Found: 2.11.

Calc. for  $C_{15}H_{14}O_6N_3As$ : N, 10.74. Found: 10.83.

**Diazobenzene - (4-arsonic acid) - 4' - amino-phenylarsonic acid.**—The diazo solution from 4.4 g. of arsanilic acid was treated with 4.4 g. of arsanilic acid in 40 cc. of *N* sodium hydroxide solution. The monosodium salt crystallized on rubbing. From 50% alcohol it forms thin, yellow, lustrous platelets which dissolve appreciably in water.

*Analyses.* Calc. for  $C_{12}H_{12}O_6N_3As_2Na \cdot 2.5H_2O$ :  $H_2O$ , 8.79. Found: 9.47.

Calc. for  $C_{12}H_{12}O_6N_3As_2Na$ : N, 8.99. Found: 9.01.

In 1 mol. of normal sodium hydroxide it yields the disodium salt on addition of sodium acetate, separating from 50% alcohol as woolly masses of delicate yellow needles which dissolve quite readily in water.

*Analyses.* Calc. for  $C_{12}H_{11}O_6N_3As_2Na_2 \cdot 7H_2O$ :  $H_2O$ , 20.49. Found: 20.18.

Calc. for  $C_{12}H_{11}O_6N_3As_2Na_2$ : N, 8.59. Found: 8.61.

The arsonic acid, precipitated from dilute aqueous solution, separates from 95% alcohol as pale yellow aggregates of microscopic needles which intumesce at 154° with preliminary darkening and sintering.

*Analyses.* Calc. for  $C_{12}H_{13}O_6N_3As_2$ : N, 9.44; As, 33.68. Found: N, 9.17; As, 33.84.

#### (D) Diazo-amino Compounds of Arsanilic Acid with Aryl Glycines.

**Diazobenzene - (4-arsonic acid) - phenylglycine.**—Alcoholic B  $\rightarrow$  neutralized A gave a thick slurry of the red-brown monosodium salt. The collected salt was dissolved in 10 parts of 50% alcohol with sodium hydroxide and the filtrate treated with a slight excess of acetic acid, slowly separating as flat, brown-yellow microscopic needles which are sparingly soluble in cold water. The free acid could not be obtained crystalline. The properties of the substance show that it is a true diazo-amino compound, but its color and that of its solutions indicate that it is contaminated with the corresponding azo dye, especially as Mai<sup>6</sup> obtained dyes on using phenylglycine as a coupler in mineral acid solution.

<sup>6</sup> Mai, *Ber.*, 35, 580 (1902).

*Analyses.* Calc. for  $C_{14}H_{18}O_6N_3AsNa \cdot 2H_2O$ :  $H_2O$ , 8.24. Found: 7.21.

Calc. for  $C_{14}H_{18}O_6N_3AsNa$ : N, 10.47; As, 18.70. Found: N, 10.22; As, 18.90.

**Diazobenzene - (4-arsonic acid) - *p* - tolylglycine.**—B + 1 mol. alkali  $\rightarrow$  A + sodium acetate, gave the monosodium salt, which was dissolved in dil. sodium hydroxide solution, treated with saturated sodium acetate solution, and then with an excess of acetic acid. The pure salt crystallized as radiating masses of tan, microscopic needles which are difficultly soluble in cold water.

*Analyses.* Calc. for  $C_{15}H_{18}O_6N_3AsNa \cdot 1.5H_2O$ :  $H_2O$ , 6.11. Found: 6.83.

Calc. for  $C_{15}H_{18}O_6N_3AsNa$ : N, 10.12; As, 18.06. Found: N, 10.07; As, 17.68.

When liberated in 50% alcohol the acid separates as radiating masses of flat, pale terra-cotta-colored microscopic needles which intumesce at  $148-9^\circ$  with preliminary softening and reddening, and are appreciably soluble in alcohol.

*Analysis.* Calc. for  $C_{15}H_{18}O_6N_3As$ : N, 10.69. Found: 10.77.

**Diazobenzene - (4-arsonic acid) - benzylglycine.**—B + mol. alkali  $\rightarrow$  neutralized A followed by hydrochloric acid. The precipitate was dissolved in warm alcohol and water added to incipient turbidity, the arsonic acid separating as an almost colorless, glistening mass of branched and curved microscopic needles and prisms which intumesce at  $155-60^\circ$ . It is readily soluble in methyl alcohol.

*Analyses.* Calc. for  $C_{15}H_{18}O_6N_3As$ : N, 10.68; As, 19.07. Found: N, 10.68; As, 19.05.

**Diazobenzene - (4-arsonic acid) - 4'-methoxy-phenylglycine ethyl ester.**—Alcoholic B  $\rightarrow$  neutralized A + equal volume of alcohol, followed by sodium acetate, gave the sodium salt which separates from 85% alcohol as yellow-brown leaflets and flat needles which are easily soluble in water. The acid could not be obtained crystalline.

*Analyses.* Calc. for  $C_{17}H_{19}O_6N_3AsNa \cdot 4H_2O$ :  $H_2O$ , 13.55. Found: 13.79.

Calc. for  $C_{17}H_{19}O_6N_3AsNa$ : N, 9.15. Found: 9.05.

**Diazobenzene - (4-arsonic acid) - 4'-methoxy-phenylglycine.**—B + 1 mol. alkali  $\rightarrow$  neutralized A, on chilling in a freezing mixture, treating with an excess of acetic acid, and rubbing, gave the monosodium salt as a highly colored powder. Redissolved in dil. sodium hydroxide solution and acidified with acetic acid, it separated as yellow, microscopic platelets which are sparingly soluble in cold water, but dissolve on gentle warming, forming reddish solutions. The acid could not be made to crystallize. The salt was also obtained by saponification of the ethyl ester described above.

*Analyses.* Calc. for  $C_{15}H_{18}O_6N_3AsNa \cdot 2H_2O$ :  $H_2O$ , 7.71. Found: 6.98.

Calc. for  $C_{15}H_{18}O_6N_3AsNa$ : N, 9.74; As, 17.39. Found: N, 9.79; As, 17.16.

**Diazobenzene - (4-arsonic acid) - 4'-ethoxy-phenylglycine ethyl ester.**—Obtained as in the preceding case, the sodium salt separates from 70% alcohol as lustrous, cream-colored leaflets.

*Analyses.* Calc. for  $C_{15}H_{21}O_6N_3AsNa \cdot 2.5H_2O$ :  $H_2O$ , 8.69. Found: 8.78.

Calc. for  $C_{15}H_{21}O_6N_3AsNa$ : N, 8.88. Found: 9.05.

Liberated from 25% alcoholic solution, the acid forms almost colorless microscopic rhombohedra.

**Diazobenzene - (4-arsonic acid) - 4'-ethoxy-phenylglycine.**—On saponifying the ester in 2 mols. of N sodium hydroxide solution at room temperature, adding a little sodium acetate, and then an excess of acetic acid with chilling, the monosodium salt of the glycine arsonic acid crystallized as aggregates of thin, yellow, microscopic needles which are sparingly soluble in water. The free acid could not be obtained crystalline.

*Analyses.* Calc. for  $C_{15}H_{17}O_6N_3AsNa \cdot 2H_2O$ :  $H_2O$ , 7.48. Found: 6.49.

Calc. for  $C_{15}H_{17}O_6N_3AsNa$ : N, 9.44; As, 16.85. Found: N, 9.54; As, 16.63.

This salt was also obtained directly from the diazo solution and *p*-ethoxy-phenylglycine, as in the case of the *p*-methoxy compound.

## (E) Diazo-amino Compounds of the Amino-phenoxyacetic Acids.

**Diazobenzene - (4-arsonic acid) - 4'- amino-phenoxyacetic ethyl ester.**—B hydrochloride  $\rightarrow$  neutralized A, half saturated with sodium acetate, gave the sodium salt which forms brownish aggregates of microscopic needles from 85% alcohol.

*Analyses.* Calc. for  $C_{16}H_{17}O_6N_3AsNa \cdot 5H_2O$ :  $H_2O$ , 16.83. Found: 17.04.

Calc. for  $C_{16}H_{17}O_6N_3AsNa$ : N, 9.44; As, 16.83. Found: N, 9.84; As, 16.99.

Liberated in 50% alcoholic solution, the ester acid forms salmon-colored, minute, glistening leaflets which melt and decompose at  $132-3^\circ$  with preliminary softening and dissolve readily in warm methyl and ethyl alcohols.

*Analysis.* Calc. for  $C_{16}H_{15}O_6N_3As$ : N, 9.93. Found: 9.76.

**Diazobenzene - (4-arsonic acid) - 4'- amino-phenoxyacetic acid.**—Although this substance was prepared directly from *p*-amino-phenoxyacetic acid<sup>7</sup> it was found preferable to saponify the above ester. The ester salt was warmed gently for one hour with 2 mols. of *N* sodium hydroxide solution and an equal volume of alcohol, chilled, neutralized with acetic acid, and the crude disodium salt precipitated with alcohol. It forms brown needles from 85% alcohol which gradually darken and decompose on standing.

*Analyses.* Calc. for  $C_{14}H_{12}O_6N_3AsNa_2 \cdot 6.5H_2O$ :  $H_2O$ , 21.05. Found: 21.35.

Calc. for  $C_{14}H_{12}O_6N_3AsNa_2$ : N, 9.56. As, 17.07. Found: N, 9.58; As, 17.06.

A well chilled solution in 100 parts of water was strongly acidified with acetic acid, causing the sudden incomplete separation of the free arsonic acid as aggregates of microscopic crystals. The cold mixture was just acidified to congo red and filtered cold, for if allowed to warm the acid rapidly dissociates and dissolves. It melts and intumesces at  $132^\circ$ .

*Analysis.* Calc. for  $C_{14}H_{14}O_6N_3As$ : N, 10.64. Found: 10.41.

**Diazobenzene - (4-arsonic acid) - *p* - amino-phenoxyacetamide.**—Aqueous *p*-amino-phenoxyacetamide<sup>8</sup>  $\rightarrow$  neutralized A, half saturated with sodium acetate, gave the sodium salt in excellent yield. It separates from 50% alcohol as rosetts and sheaves of delicate, drab-colored needles which dissolve fairly readily in water.

*Analyses.* Calc. for  $C_{14}H_{14}O_6N_4AsNa \cdot 6H_2O$ :  $H_2O$ , 20.62. Found: 19.88.

Calc. for  $C_{14}H_{14}O_6N_4AsNa$ : N, 13.46; As, 18.02. Found: N, 13.72; As, 17.56.

The arsonic acid, obtained from the salt in 50% alcohol, formed branched aggregates of cream-colored, microscopic needles and hairs which melt and effervesce at about  $162^\circ$  with preliminary browning.

*Analysis.* Calc. for  $C_{14}H_{16}O_6N_4As$ : N, 14.22. Found: 14.09.

**Diazobenzene - (4-arsonic acid) - *p* - amino-phenoxyacet-methylamide.**—The amorphous salt from *p*-amino-phenoxyacet-methylamide<sup>9</sup> soon crystallized, separating from water as pale yellow aggregates of hair-like needles.

*Analyses.* Calc. for  $C_{15}H_{16}O_6N_4AsNa \cdot 4H_2O$ :  $H_2O$ , 14.34. Found: 14.60.

Calc. for  $C_{15}H_{16}O_6N_4AsNa$ : N, 13.02; As, 17.43. Found: N, 12.94; As, 17.77.

The free arsonic acid from a dilute, 50% alcoholic solution of the salt, forms minute, flat, glistening cream-colored needles which melt with decomposition at  $170^\circ$  with preliminary darkening.

*Analyses.* Calc. for  $C_{15}H_{17}O_6N_4As \cdot H_2O$ :  $H_2O$ , 4.23. Found: 3.66.

Calc. for  $C_{15}H_{17}O_6N_4As$ : N, 13.73. Found: 13.33.

**Diazobenzene - (4-arsonic acid) - 4'- methylamino-phenoxyacetic acid.**—Coupled in neutral solution and then acidified strongly with acetic acid, *p*-*N*-methylamino-phenoxyacetic acid<sup>10</sup> gave the diazo-amino acid which, on redissolving in dil. alkali and

<sup>7</sup> THIS JOURNAL, 39, 2196 (1917).

<sup>8</sup> *Ibid.*, 39, 2423 (1917).

<sup>9</sup> *Loc. cit.*, p. 2424.

<sup>10</sup> *Ibid.*, 39, 2197 (1917).

reprecipitating with acetic acid in excess, forms greenish-yellow aggregates of microscopic spindles which decompose at 155–60°.

*Analyses.* Calc. for  $C_{16}H_{16}O_6N_3As$ : N, 10.26; As, 18.32. Found: N, 10.47; As, 18.50.

**Diazobenzene - (4-arsonic acid) - 3'-methyl-4'-amino-phenoxyacetic methyl ester.**—In neutral solution, in the presence of sodium acetate, the amino ester hydrochloride<sup>11</sup> gave the sodium salt as a thick mass of reddish-brown, microscopic needles. In 50% alcohol, acetic acid precipitates the acid as rosetts of minute needles, melting and decomposing at 105–7°.

*Analysis.* Calc. for  $C_{16}H_{16}O_6N_3As$ : N, 9.93. Found: 9.83.

**Diazobenzene - (4-arsonic acid) - 3'-methyl-4'-amino-phenoxyacetic acid.**—The ester was saponified and the disodium salt isolated as in previous examples. Dissolved in a small volume of water and treated with alcohol it crystallized as light brown, glistening plates containing water of crystallization which was not determined. The free acid proved too unstable for isolation.

*Analyses.* Calc. for  $C_{16}H_{14}O_6N_3AsNa_2$ : N, 9.27; As, 16.55. Found: N, 9.04; As, 16.32.

**Diazobenzene - (4-arsonic acid) - 2'-methyl-4'-amino-phenoxyacetic methyl ester.**—The sodium salt, obtained from the amino ester hydrochloride,<sup>12</sup> gave with acetic acid in 50% alcohol the acid as aggregates of round, purple-brown, microscopic leaflets which decompose at 143–4° and dissolve in hot methyl and ethyl alcohols.

*Analysis.* Calc. for  $C_{16}H_{16}O_6N_3As$ : N, 9.93. Found: 9.81.

**Diazobenzene-(4-arsonic acid) - 2' - methyl-4'-amino-phenoxyacetic acid.**—The disodium salt obtained from the ester crystallized from dil. alcohol as easily soluble, long, flat, pinkish-yellow, microscopic needles which gradually decomposed on exposure. The acid proved to be too unstable for isolation.

*Analyses.* Calc. for  $C_{16}H_{14}O_6N_3AsNa_2 \cdot 4.5H_2O$ :  $H_2O$ , 15.16. Found: 15.42.

Calc. for  $C_{16}H_{14}O_6N_3AsNa_2$ : N, 9.27; As, 16.55. Found: N, 9.50; As, 16.81.

**Diazobenzene - (4-arsonic acid) - 2',5'-dimethyl-4'-amino-phenoxyacetic methyl ester.**—Amino ester hydrochloride<sup>13</sup> in 50% alcohol  $\rightarrow$  A, followed by sodium acetate. Addition of an equal volume of alcohol to the thick amorphous slurry gave the microcrystalline ester acid which was dissolved in warm 50% alcohol with ammonia, diluted with several volumes of alcohol, chilled, and acidified with acetic acid, crystallizing as gray-yellow aggregates of short, flat, pointed microscopic needles. It decomposes at about 120° and is quite soluble in hot methyl alcohol.

*Analyses.* Calc. for  $C_{17}H_{20}O_6N_3As \cdot 1.5H_2O$ :  $H_2O$ , 5.82. Found: 5.89.

Calc. for  $C_{17}H_{20}O_6N_3As$ : N, 9.61; As, 17.15. Found: N, 9.69; As, 17.35.

On saponifying the ester what was presumably the disodium salt of the acid was obtained as pale yellow needles, but all attempts to obtain an analytically pure sample of the salt as well as of the free acid proved futile.

**Diazobenzene-(4-arsonic acid)-2'-methyl-5'-isopropyl-4'-amino-phenoxyacetic methyl ester.**—Amino ester hydrochloride<sup>14</sup> A  $\rightarrow$  + sodium acetate, followed by alcohol gave the ester acid, which, reprecipitated from ammoniacal 50% alcoholic solution, formed microscopic needles which decompose at 145° and are appreciably soluble in hot alcohol.

*Analysis.* Calc. for  $C_{19}H_{24}O_6N_3As$ : N, 9.03. Found: 9.16.

**Diazobenzene-(4-arsonic acid)-2'-methyl-5'-isopropyl-4'-amino-phenoxyacetic acid.**

<sup>11</sup> *Loc. cit.*, p. 2201.

<sup>12</sup> *Ibid.*, p. 2199.

<sup>13</sup> *Ibid.*, p. 2205.

<sup>14</sup> *Ibid.*, p. 2206.

—The ester was saponified as usual, yielding the disodium salt. Dissolved in a small volume of water and treated with alcohol it formed minute, flat, pale brown needles.

*Analyses.* Calc. for  $C_{13}H_{20}O_6N_3AsNa_2 \cdot 9.5H_2O$ :  $H_2O$ , 25.68. Found: 25.39.

Calc. for  $C_{13}H_{20}O_6N_3AsNa_2$ : N, 8.49; As, 15.14. Found: N, 8.24; As, 15.05. All attempts to obtain the free acid failed.

**Diazobenzene - (4-arsonic acid) - 3'-methyl-6'-isopropyl-4'-amino-phenoxyacetic methyl ester.**—Prepared from the ester hydrochloride<sup>15</sup> as in the case of the 2,5-dimethyl analog. Recrystallized from 85% alcohol the acid formed rosetts of yellow microscopic leaflets. When rapidly heated it intumesces to an orange mass at about 130°, but if slowly heated it turns orange above 120°, then gradually darkens, but does not melt below 275°.

*Analyses.* Calc. for  $C_{19}H_{24}O_6N_3As \cdot 1.5H_2O$ :  $H_2O$ , 5.49. Found: 4.56.

Calc. for  $C_{19}H_{24}O_6N_3As$ : N, 9.03. Found: 8.92.

**Diazobenzene - (4-arsonic acid) - 3'-methyl-6'-isopropyl-4'-amino-phenoxyacetic acid.**—The crude disodium salt from the ester was reprecipitated from a little water by alcohol, separating as lustrous yellow microscopic leaflets.

*Analyses.* Calc. for  $C_{18}H_{20}O_6N_3AsNa_2 \cdot 4H_2O$ :  $H_2O$ , 12.69. Found: 12.26.

Calc. for  $C_{18}H_{20}O_6N_3AsNa_2$ : N, 8.49; As, 15.14. Found: N, 8.36; As, 14.67. The acid could not be isolated.

**Diazobenzene-(4-arsonic acid) -2'-bromo-4'-amino-phenoxyacetic methyl ester.**—

The ester acid from 2-bromo-4-amino-phenoxyacetic methyl ester hydrochloride<sup>16</sup> was reprecipitated from very dilute aqueous ammonia, forming a jelly which changed to long, curved, cream-colored, microscopic needles which decompose at 154–5°.

*Analysis.* Calc. for  $C_{15}H_{15}O_6N_3BrAs$ : N, 8.61. Found: 8.71.

**Diazobenzene -(4-arsonic acid) -2'-bromo-4'-amino-phenoxyacetic acid.**—The disodium salt obtained from the ester was recrystallized as usual, forming flat, lustrous, pale brownish-yellow needles.

*Analyses.* Calc. for  $C_{14}H_{11}O_6N_3BrAsNa_2 \cdot 4H_2O$ :  $H_2O$ , 12.20. Found: 12.44.

Calc. for  $C_{14}H_{11}O_6N_3BrAsNa_2$ : N, 8.11; As, 14.47. Found: N, 8.26; As, 14.71.

On acidifying an aqueous solution of the salt to congo red, a thick jelly formed, which, on addition of alcohol changed to delicate, pale yellow, microscopic needles which decompose at about 120° when anhydrous.

*Analyses.* Calc. for  $C_{14}H_{13}O_6N_3BrAs \cdot 3H_2O$ :  $H_2O$ , 10.22. Found: 9.41.

Calc. for  $C_{14}H_{13}O_6N_3BrAs$ : N, 8.86. Found: 9.03.

**Diazobenzene - (4-arsonic acid) - 2-methyl-4-amino-6-bromo-phenoxyacetic methyl ester.**—Amino ester hydrochloride<sup>17</sup> in 50 % alcohol neutralized  $\rightarrow$  A + sodium acetate. The yellow diazo-amino sodium salt, in ammoniacal dil. alcoholic solution, was acidified with acetic acid, yielding the free ester arsonic acid as bundles of delicate, pinkish, microscopic needles which intumesce at 188°.

*Analyses.* Calc. for  $C_{18}H_{17}O_6N_3BrAs$ : N, 8.37; As, 14.92. Found: N, 8.36; As, 15.15.

**Diazobenzene-(4-arsonic acid)-2-methyl-4-amino-6-bromo-phenoxyacetic acid.**

—The disodium salt was obtained as an indefinitely crystalline product and was dried *in vacuo*. It dissolves easily in water with a deep orange color.

*Analyses.* Calc. for  $C_{18}H_{15}O_6N_3BrAsNa_2$ : N, 7.90; As, 14.08. Found: N, 7.75; As, 13.42.

In dilute 50% alcoholic solution the salt yielded the free acid as grayish, micro-

<sup>15</sup> *Loc. cit.*, p. 2207.

<sup>16</sup> *Ibid.*, p. 2209.

<sup>17</sup> *Ibid.*, 39, 2211 (1917).

crystalline aggregates which decompose at about 155°, with preliminary darkening and softening.

**Diazobenzene - (4-arsonic acid) -4'- amino-6'-aceto-phenoxyacetic methyl ester.**—The methyl ester hydrochloride<sup>18</sup>  $\rightarrow$  A + 1 mol. sodium hydroxide, followed by sodium acetate. The free acid, obtained from a dilute 50% alcoholic solution of the salt, was dissolved in 50% alcohol with a little aqueous ammonia and precipitated with a large excess of acetic acid, separating as rosetts and sheaves of microscopic, often hair-like needles. It effervesces and reddens at about 155°, with preliminary darkening.

*Analysis.* Calc. for  $C_{17}H_{18}N_7O_3As$ : N, 9.81. Found: 9.64.

**Diazobenzene - (4-arsonic acid) -4'- amino-6'-aceto-phenoxyacetic acid.**—The disodium salt separated on adding alcohol to its aqueous solution as pale brown, microscopic leaflets. The free acid was not obtained pure.

*Analyses.* Calc. for  $C_{16}H_{14}O_7N_3AsNa_2 \cdot 5H_2O$ :  $H_2O$ , 15.77. Found: 16.36.

Calc. for  $C_{16}H_{14}O_7N_3AsNa_2$ : N, 8.73; As, 15.58. Found: N, 8.88; As, 15.50.

**Diazo-2-methylbenzene-(4-arsonic acid) - p - amino-phenoxyacetic methyl ester.**—o-Methylarsanilic acid was diazotized in the same way as arsanilic acid and the solution treated first with a large excess of saturated sodium acetate solution and then with an equivalent of p-amino-phenoxyacetic methyl ester hydrochloride<sup>19</sup> dissolved in water. The initially amorphous diazo-amino sodium salt crystallized on letting stand in the cold as spherules of drab, microscopic needles. The free ester acid forms sheaves, rosetts, and plumes of minute, flat needles which decompose at 130-2°.

*Analysis.* Calc. for  $C_{16}H_{18}O_6N_3As$ : N, 9.93. Found: 10.02.

**Diazo - 2 - methylbenzene - (4-arsonic acid) - p - amino-phenoxyacetic acid.**—The ester, saponified as usual, yielded the disodium salt which separated from aqueous solution on adding alcohol as radiating masses of minute, brownish leaflets. The free acid was not obtained crystalline.

*Analyses.* Calc. for  $C_{15}H_{14}O_6N_3AsNa_2 \cdot 6.5H_2O$ :  $H_2O$ , 20.53. Found: 20.80.

Calc. for  $C_{15}H_{14}O_6N_3AsNa_2$ : N, 9.27; As, 16.55. Found: N, 9.02; As, 16.64.

**Diazo - 2 - bromobenzene - (4-arsonic acid) - p - amino-phenoxyacetic methyl ester.**—4.5 g. of 3-bromo-arsanilic acid<sup>20</sup> were suspended in 30 cc. of 2 N hydrochloric acid, diazotized with 1.1 g. of sodium nitrite, and the solution chilled and treated with 22.5 cc. of 2 N sodium hydroxide, then with an equal volume of saturated sodium acetate solution and finally with a solution of 3.3 g. of the amino ester hydrochloride. The diazo-amino ester salt separated immediately as aggregates of pinkish, hair-like, microscopic needles. The ester acid forms spherules of brownish, microscopic needles which intumesce at 123-5°.

*Analysis.* Calc. for  $C_{15}H_{15}O_6N_3BrAs$ : N, 8.61. Found: 8.49.

**Diazo - 2 - bromobenzene - (4-arsonic acid) - p - amino-phenoxyacetic acid.**—The recrystallized disodium salt of the acid separates as drab-colored spherules of minute crystals.

*Analyses.* Calc. for  $C_{14}H_{11}O_6N_3BrAsNa_2 \cdot 4H_2O$ :  $H_2O$ , 13.19. Found: 13.77.

Calc. for  $C_{14}H_{11}O_6N_3BrAsNa_2$ : N, 8.11; As, 14.47. Found: N, 7.88; As, 14.28.

The free arsonic acid is precipitated from 50% alcohol as drab microscopic crystals which intumesce slowly at about 130° with preliminary browning.

*Analyses.* Calc. for  $C_{14}H_{13}O_6N_3BrAs$ : N, 8.87; As, 15.80. Found: N, 8.80; As, 15.77.

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<sup>18</sup> *Loc. cit.*, p. 2215.

<sup>19</sup> *Ibid.*, p. 2196.

<sup>20</sup> Berthelm, *Ber.*, 43, 532 (1910).

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

## AROMATIC ARSENIC COMPOUNDS. X. AZO DYES DERIVED FROM ARSANILIC ACID.

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Received June 29, 1920.

As stated in the previous paper, azo dyes containing arsenic were first described by Ehrlich and Bertheim<sup>1</sup> and later by Barrowcliff, Pyman, and Remfry,<sup>2</sup> and others. In our work with diazo-amino derivatives it was found that certain classes of aromatic amino compounds yielded amino-azo dyes at once when used as couplers with diazotized arsanilic acid, or gave diazo-amino compounds which rapidly rearranged into the dyes. This occurred with *N*-alkyl anthranilic acids, *m*-amino-phenoxyacetic acid and its substitution products, the amino-veratric acids, and the *o*-methyl and *o*-alkoxy derivatives of *N*-phenylglycine.

As far as we can find, no mention has been made of the use of *N*-alkyl-anthranilic acids for the synthesis of azo dyes. The addition of *N*-methyl anthranilic acid to the neutralized diazo solution results in the rapid formation first of the diazo-amino compound, which slowly rearranges to the dye on standing or changes over rapidly on acidification with acetic acid. A similar behavior was noted with *N*-ethyl- and *N*-iso-amyl-anthranilic acids.

Under the usual conditions of coupling in neutral or slightly acid solution, *m*-amino-phenoxyacetic acid yielded at once a dye in which we assume the azo group to enter the position *para* to the amino group. We believe that *m*-amino-phenoxyacetic acid functions here as a *m*-anisidine derivative as we have since noted the analogous experience of Reverdin, Rilliet and Vernei,<sup>3</sup> in which *p*-amino-azo dyes were prepared from *m*-phenetidine. Azo derivatives were also obtained by us from two groups of substitution products of *m*-anisidine and *m*-amino-phenoxyacetic acid, in one of which the position *para* to the amino group was free, and in the other of which this position was occupied by a substituent. In the former group were 4-methyl-5-amino-phenoxyacetic acid and 2-amino-3,4-dimethoxy-benzoic acid, and in these cases the azo group presumably entered the free *para* position. In the second group were 2-methyl-5-amino-phenoxyacetic acid, 3-amino-6-methoxy-phenoxyacetic acid, 6-amino-*o*-veratric acid, 4-amino-6-methoxy-phenoxyacetic acid, and amino-*o*-phenylene-di (oxyacetic acid); and in this group it is probable that the azo group enters the position *ortho* to the amino group. Thus German patent 230,592 describes the formation of *o*-amino-azo dyes

<sup>1</sup> Ehrlich and Bertheim, *Ber.*, 40, 3292 (1907).

<sup>2</sup> Barrowcliff, Pyman and Remfry, *J. Chem. Soc.*, 93, 1893 (1908).

<sup>3</sup> *C. A.*, 13, 312 (1919).



from 2-methyl-5-amino-phenoxyacetic acid and from the analogous 2-methyl-5-amino-anisole, and our experience has confirmed the ready formation of azo dyes from such substances.

Finally, although phenylglycine yields principally a diazo-amino compound under the conditions described in the preceding paper, the *o*-methyl, *o*-methoxy, and *o*-ethoxyphenyl glycines at once form dyes. According to Mai,<sup>4</sup> however, when phenylglycine was coupled in a solution acid to congo red it yielded dyes with diazotized aniline and sulfanilic acid.

In most cases the reaction between the diazotized arsanilic acid and the coupler proceeded smoothly, with very little gas evolution. The isolation and purification of the resulting dyes often presented considerable difficulty, and much experimentation was necessary in order to discover the best conditions for the coupling and whether any dye were best isolated as the free acid, the monosodium salt, or the disodium salt. Hence the manipulative details are quite voluminous, and in order to save space it is deemed best to present the work in abstract form.

The monosodium salts of the dyes were generally very sparingly soluble in water, while the disodium salts dissolved easily. Even very dilute solutions of the latter gave immediate amorphous precipitates with salts of the heavier metals, while their behavior varied toward salts of the alkaline earths.

### Experimental.

To avoid constant repetition it may be stated here that the diazotization of arsanilic acid was carried out under the conditions given in the preceding paper in 2 mols. of normal hydrochloric acid with 5 *N* sodium nitrite. Since most of the amino acids were coupled under the conditions necessary for the formation of the monosodium salts of the resulting dyes, it will be understood unless otherwise stated that the diazo solution was first treated with one mol. of *N* sodium hydroxide solution, the solution thus containing diazobenzene arsonic acid and no free mineral acid. This solution was then slowly treated, with continued turbinizing and chilling, with a solution of the amino acid dissolved in one mol. of *N* sodium hydroxide solution, or treated with an additional mol. of alkali and then with a solution of the coupler hydrochloride in the case of basic couplers. Such a procedure will be indicated by the expression  $B \rightarrow A$ . Cases in which the diazo solution was added to the coupler are designated by  $A \rightarrow B$ . Variations from this procedure will be described as they occur.

The values given for water of crystallization were determined on the substances after they had come to equilibrium in the air.

<sup>4</sup> Mai, *Ber.*, 35, 580 (1902).

**(A) Dyes Derived from Arsanilic Acid and Methoxy-naphthylamines.**

**1-Amino-2-methoxy-naphthalene-4'-azobenzene-4'-arsonic acid.**—**B**  $\longrightarrow$  **A**, using  $\beta$ -methoxy- $\alpha$ -naphthylamine hydrochloride. The neamorphous acid was converted into the salt with just enough dil. sodium hydroxide solution. After salting out, dissolving in 50% alcohol, heating, and making just acid to congo red with hydrochloric acid, the arsonic acid slowly separated on rubbing and cooling as radiating aggregates of narrow, bluish-black, glistening, microscopic platelets, which did not melt below 285°. It dissolves in conc. sulfuric acid with a deep purple color and in dil. sodium hydroxide solution with a deep cherry-red tint.

*Analyses.* Calc. for  $C_{17}H_{16}O_4N_3As \cdot 1.5H_2O$ :  $H_2O$ , 6.3. Found: 5.9.

Calc. for  $C_{17}H_{16}O_4N_3As$ : N, 10.48; As, 18.68. Found: N, 10.42; As, 18.50.

**1-Amino-4-methoxy-naphthalene-2-azobenzene-4'-arsonic acid.**—Obtained like the preceding compound, the arsonic acid separated rapidly as dark brown, microcrystalline aggregates with a bronzy luster. It sintered and darkened when heated, softening to a tar at about 195° and intumescing at about 225°. It dissolves in conc. sulfuric acid with a purplish-red color, changing to brown-red, and becoming purplish again on dilution. In dil. sodium hydroxide solution the color is a deep cherry-red. It is soluble in acetic acid and alcohol.

*Analyses.* Calc. for  $C_{17}H_{16}O_4N_3As \cdot 1.5H_2O$ :  $H_2O$ , 6.3. Found: 6.0.

Calc. for  $C_{17}H_{16}O_4N_3As$ : N, 10.48; As, 18.68. Found: N, 10.31; As, 18.83.

**(B) Dyes Obtained from Arsanilic Acid and Substituted Amino-benzoic Acids.**

**4-Methylamino-5-carboxy-phenylazo-benzene-4'-arsonic acid.**—**B** (methylantranilic acid)  $\longrightarrow$  **A** + equal volume saturated sodium acetate solution. The orange colored solution, which presumably contained the diazo-amino compound, deepened in color on standing, gradually depositing the orange monosodium salt in good yield. Recrystallized from boiling water containing a little sodium acetate, it forms radiating masses of short, brownish-yellow, microscopic needles which dissolve with difficulty in hot or cold water with an intense orange-yellow color.

*Analyses.* Calc. for  $C_{14}H_{13}O_5N_3AsNa \cdot 2.5H_2O$ :  $H_2O$ , 10.08. Found: 10.49.

Calc. for  $C_{14}H_{13}O_5N_3AsNa$ : N, 10.47. Found: 10.53.

Treated in a little water with one mol. of sodium hydroxide, then with alcohol to initial turbidity, the disodium salt separated in the cold. It forms bundles of flat, red, microscopic needles from 70% alcohol and dissolves readily in water with a deep orange color.

*Analyses.* Calc. for  $C_{14}H_{13}O_5N_3AsNa_2 \cdot 8.5H_2O$ :  $H_2O$ , 26.57. Found: 26.63.

Calc. for  $C_{14}H_{13}O_5N_3AsNa_2$ : N, 9.93. Found: N, 9.83.

The monosodium salt, suspended in hot water, dissolved with a little sodium hydroxide, and treated with hydrochloric acid until just acid to congo red, gave the free acid, which when recrystallized from 50% alcohol forms brick-red, thin, glistening microscopic needles and plates. It does not melt below 280° dissolves in conc. sulfuric acid with a deep orange color and gives a red solution in hot 10% hydrochloric acid, from which the hydrochloride separates on cooling as rosetts of narrow, purplish-red plates with a steel-blue reflex. In dil. hydrochloric acid the dye reacts with sodium nitrite, giving a precipitate of pale salmon-colored, microscopic needles, presumably the nitroso compound.

*Analyses.* Calc. for  $C_{14}H_{13}O_5N_3As$ : N, 11.08; As, 19.78. Found: N, 11.24; As, 19.68.

**4-Ethylamino-5-carboxy-phenylazo-benzene-4'-arsonic acid.**—**B**  $\longrightarrow$  **A**.—The crude monosodium salt was dissolved in hot water with a little sodium hydroxide and

the solution just acidified to congo red, yielding the bright yellow arsonic acid. It separates from 85% alcohol as deep orange, glistening rectangular platelets which do not melt below 275°. It is more soluble in methyl alcohol or boiling amyl alcohol than in the other usual neutral solvents, and in its color reactions and chemical properties resembles the methylamino compound.

*Analyses.* Calc. for  $C_{15}H_{15}O_6N_3As$ : N, 10.69; As, 19.06. Found: N, 10.72 As, 19.11.

**4 - Iso-amyl-amino - 5 - carboxy-phenylazo-benzene-4'-arsonic acid.**—B  $\longrightarrow$  A.—The crude monosodium salt when recrystallized from much water containing a little sodium acetate forms orange-colored, microscopic leaflets which are very difficultly soluble in boiling water.

*Analyses.* Calc. for  $C_{15}H_{21}O_6N_3AsNa \cdot 2H_2O$ :  $H_2O$ , 7.31. Found: 6.59.

Calc. for  $C_{15}H_{21}O_6N_3AsNa$ : N, 9.19. Found: 9.18.

Recrystallized from acetic acid, the free acid forms orange-red, glistening, striated platelets which do not melt below 275°. It dissolves in boiling alcohol and gives a deep red-orange color with conc. sulfuric acid; in conc. hydrochloric acid it dissolves with a deep red color, the hydrochloride separating on rubbing as dark colored microscopic needles.

*Analyses.* Calc. for  $C_{15}H_{20}O_6N_3As$ : N, 9.66; As, 17.22. Found: N, 9.48; As, 17.32.

**4 - Amino - 2,3 - dimethoxy-5-carboxy-phenylazo-benzene-4'-arsonic acid.**—B  $\longrightarrow$  A.—Using vicinal aminoveratric acid, the monosodium salt was obtained, separating as flat, brown-orange, microscopic needles from hot water containing a little sodium acetate.

*Analyses.* Calc. for  $C_{15}H_{15}O_7N_3AsNa \cdot 2.5H_2O$ :  $H_2O$ , 9.15. Found: 9.79.

Calc. for  $C_{15}H_{15}O_7N_3AsNa$ : N, 9.40; As, 16.77. Found: N, 9.76; As, 16.54.

The free acid separates from 85% alcohol as long, narrow, glistening, orange-red platelets which turn a deeper red when anhydrous, but do not melt below 275°. It is quite easily soluble in cold methyl alcohol and gives a deep orange-colored solution in conc. sulfuric acid, dissolving in boiling 10% hydrochloric acid with a dark red color, depositing the hydrochloride on cooling as brown platelets and flat needles.

*Analyses.* Calc. for  $C_{15}H_{15}O_7N_3As \cdot 1.5H_2O$ :  $H_2O$ , 5.98. Found: 6.43.

Calc. for  $C_{15}H_{15}O_7N_3As$ : As, 17.62. Found: As, 17.78.

**2 - Amino - 4,5 - dimethoxy-3-carboxy-phenylazo-benzene-4'-arsonic acid.**—(B  $\longrightarrow$  A.—Alkalinity sufficient for formation of the disodium salt.) 6-Amino-*o*-veratric acid<sup>5</sup> was used. After 24 hours about 20% of solid sodium acetate was added and then an excess of acetic acid, precipitating the monosodium salt. Recrystallized from water containing sodium acetate, cautiously adding acetic acid after cooling, the salt forms spherules of orange-red microcrystals which change to chocolate-brown when air-dry. It is very difficultly soluble in boiling water and dissolves on adding alkali with an orange color.

*Analyses.* Calc. for  $C_{15}H_{15}O_7N_3AsNa \cdot 1.5H_2O$ :  $H_2O$ , 5.70. Found: 6.37.

Calc. for  $C_{15}H_{15}O_7N_3AsNa$ : N, 9.40; As, 16.77. Found: N, 9.21; As, 16.65

The free acid separates from an alkaline solution of the salt in 50% alcohol on acidifying to congo red as glistening brown leaflets and microcrystalline aggregates with a purplish luster, containing about 1.5 molecules of water of crystallization and turning darker brown when dehydrated. It decomposes somewhat on heating, but does not melt up to 290°. It is difficultly soluble in the usual solvents, and unlike the monosodium salt, dissolves in dil. alkalis with a red color, only changing to orange at high dilution. It gives an intense red color in conc. sulfuric acid, and dissolves partially in conc. hydro-

<sup>5</sup> This acid was prepared by the following series of reactions, which will be dealt with in a later communication: *o*-vanillin  $\longrightarrow$  *o*-veratric aldehyde  $\longrightarrow$  6-nitro-*o*-veratric aldehyde  $\longrightarrow$  6-nitro-*o*-veratric acid  $\longrightarrow$  6-amino-*o*-veratric acid.

chloric acid, the hydrochloride soon separating as dark orange-red microcrystalline spherules.

*Analyses.* Calc. for  $C_{15}H_{16}O_7N_3As \cdot 1.5H_2O$ :  $H_2O$ , 5.98. Found: 5.29.

Calc. for  $C_{15}H_{16}O_7N_3As$ : N, 9.89. Found: 9.69.

### (C) Dyes Derived from Arsanilic Acid and Aromatic Glycines.

**4-[Phenyl - (4'-arsonic acid) azo] - phenylglycine.**—Although phenylglycine yielded the diazo-amino compound under the conditions given in the preceding paper, the dye was formed in the presence of an excess of mineral acid. The diazo solution from 4.4 g. of arsanilic acid was added, with stirring and chilling, to a solution of 3.1 g. of phenylglycine in 40 cc. of *N* hydrochloric acid diluted to 100 cc. with 0.5 *N* hydrochloric acid. The dye, which crystallized soon after deposition commenced, was filtered off, washed first with cold and then with hot water, and was finally cooled and washed with acetone. The yield was 5.3 g. A dilute solution in 50% alcohol was obtained with the aid of a little ammonia and acidified hot to congo red, the arsonic acid soon separating as orange-red aggregates of minute, lenticular platelets with a golden luster. It sinters, melts, and decomposes slowly at 170–5°, and dissolves in dil. alkali with a reddish-orange color. It dissolves in conc. sulfuric acid or 1 : 1 hydrochloric acid with a deep red color, the hydrochloride separating from the latter on rubbing as red microscopic needles with a purplish luster.

*Analyses.* Calc. for  $C_{14}H_{14}O_5N_3As \cdot 0.5H_2O$ :  $H_2O$ , 2.32. Found: 2.86.

Calc. for  $C_{14}H_{14}O_5N_3As$ : N, 11.07. Found: 11.43.

**2 - Methyl - 4 - [phenyl - (4'-arsonic acid) azo] phenylglycine.**—(A unneutralized  $\rightarrow$  B in 2 mols. of alkali.) The dye salt separated on rubbing and was dissolved in 50% alcohol with the aid of sodium hydroxide and the red-orange solution then made just acid to congo red, the arsonic acid separating as red-brown needles, leaflets, and rhombic platelets. When rapidly heated to 155°, then slowly, the acid reddens and intumesces at 157°. It is quite soluble in the cold in methyl alcohol, and dissolves in conc. sulfuric acid with a deep red color. A solution in 1 : 1 hydrochloric acid deposits the hydrochloride on rubbing as minute, dark brown platelets with a purple luster.

*Analyses.* Calc. for  $C_{15}H_{16}O_5N_3As \cdot H_2O$ :  $H_2O$ , 4.38. Found: 3.49.

Calc. for  $C_{15}H_{16}O_5N_3As$ : N, 10.69; As, 19.06. Found: N, 10.70; As, 19.08.

**2 - Methoxy - 4 - [phenyl - (4'-arsonic acid) azo] phenylglycine.**—(B in 1 mol. of alkali  $\rightarrow$  A treated with one mol. of alkali and saturated with salt.) The monosodium salt gradually crystallized. It separates from dil. aqueous alcoholic alkali on adding acetic acid as very thin, nacreous, orange-red platelets containing about 2.5 molecules of water of crystallization when air-dry and dissolving in water with a deep red color, changing to brown and depositing microcrystalline spherules of what appears to be a different hydrate; on adding sodium acetate or sodium hydroxide a clear, deep orange solution results.

*Analyses.* Calc. for  $C_{15}H_{15}O_6N_3AsNa \cdot 2.5H_2O$ :  $H_2O$ , 9.46. Found: 8.93.

Calc. for  $C_{15}H_{15}O_6N_3AsNa$ : As, 17.39. Found: 17.28.

The acid was obtained in the usual way as minute, glistening, steel-blue aggregates of platelets. When rapidly heated the air-dry acid melts and effervesces at about 160°, but if dried first it gradually reddens on heating and intumesces at 167° to a blood-red mass. It is quite soluble in the cold in methyl alcohol, easily in hot ethyl alcohol, and dissolves in conc. sulfuric acid with a deep purple color, in 1:1 hydrochloric acid with a deep red color, and in dil. solutions of carbonates or alkalis with an orange color.

*Analyses.* Calc. for  $C_{15}H_{16}O_6N_3As \cdot 1.5H_2O$ :  $H_2O$ , 6.19. Found: 6.11.

Calc. for  $C_{15}H_{16}O_6N_3As$ : N, 10.27. Found: N, 10.30°.

**2 - Ethoxy - 4 - [phenyl - (4'-arsonic acid) azo] phenylglycine.**—On adding an equal volume of saturated sodium chloride solution to the turbid reaction mixture

the monosodium salt separated as a paste, but crystallized on rubbing. From 50% alcohol it forms rosetts of orange-brown, glistening platelets which dissolve in water with a brown-red color.

*Analyses.* Calc. for  $C_{16}H_{17}O_6N_3AsNa \cdot 2.5H_2O$ :  $H_2O$ , 9.19. Found: 8.68.

Calc. for  $C_{16}H_{17}O_6N_3AsNa$ : N, 9.44. Found: 9.63.

The free acid separates very incompletely as rosetts and sheaves of flat, purplish-brown, microscopic needles which decompose at  $245-50^\circ$  and are freely soluble in 50% alcohol and 50% acetic acid, especially on warming. The solution in conc. sulfuric acid is deep red, appearing purple in thin layers.

*Analysis.* Calc. for  $C_{16}H_{15}O_6N_3As$ : N, 9.93. Found: 10.12.

$\alpha'$ -[Phenyl - (4'-arsonic acid) azo] -  $\alpha$ -naphthylglycine.—The monosodium salt was precipitated from the reaction mixture with an equal volume of alcohol, converted into the disodium salt by dissolving in one molecular equivalent of sodium hydroxide and adding alcohol until precipitation began, purifying by redissolving in warm 50% alcohol and treating with alcohol until the concentration of solvent was about 85%, whereupon the salt crystallized. It dissolves readily in water with a purple color.

*Analyses.* Calc. for  $C_{18}H_{14}O_6N_3AsNa_2$ : N, 8.88; As, 15.85. Found: N, 9.00; As, 15.36.

The salt was dissolved in 25% alcohol, made just acid to congo red, and filtered at once from a trace of amorphous matter, after which the free acid soon crystallized. It melts and decomposes at about  $275^\circ$  with preliminary darkening and softening and dissolves in conc. sulfuric acid with a deep red color, appearing purple in thin layers.

*Analyses.* Calc. for  $C_{18}H_{14}O_6N_3As \cdot 0.5H_2O$ :  $H_2O$ , 2.1. Found: 3.0.

Calc. for  $C_{18}H_{14}O_6N_3As$ : N, 9.79. Found: 9.48.

#### (D) Dyes Derived from Arsanilic Acid and Aromatic *N*-Methyl Sulfonic Acids.

4 - [Phenyl - (4'-arsonic acid) azo] - phenyl-aminomethyl sulfonic acid,  $H_2O_3AsC_6H_4N:NC_6H_4NHCH_2SO_3H$ .—Methylene-aniline sodium bisulfite solution was added to neutralized A saturated with salt. The disodium salt of the dye soon began to crystallize on keeping in the cold, and the process was hastened by the addition of two-thirds of a volume of saturated sodium acetate solution. Recrystallized from 50% alcohol, the salt separates as delicate, orange-colored needles which dissolve readily in water.

*Analyses.* Calc. for  $C_{18}H_{15}O_6N_3SAsNa_2 \cdot 4.5H_2O$ :  $H_2O$ , 15.01. Found: 15.09.

Calc. for  $C_{18}H_{15}O_6N_3SAsNa_2$ : N, 9.15; As, 16.32. Found: N, 9.63; As, 16.78.

The salt was dissolved in 25% alcohol and the solution acidified to congo red. The acid soon separated as sheaves of minute, flat, red needles with a purplish reflex. It dissolves with difficulty in cold water, readily on boiling, with a red color. When rapidly heated to  $185^\circ$ , then slowly, the anhydrous acid turns bright red, then sinters, and finally swells and melts partially at  $187-9^\circ$ . It dissolves in conc. sulfuric acid with a transient, deep orange color, quickly fading to yellow.

*Analyses.* Calc. for  $C_{18}H_{14}O_6N_3SAs \cdot 2H_2O$ :  $H_2O$ , 7.99. Found: 8.23.

Calc. for  $C_{18}H_{14}O_6N_3SAs$ : N, 10.12; As, 18.05. Found: N, 10.30; As, 18.25.

2 - Methoxy - 4 - [phenyl - (4'-arsonic acid) azo] - phenyl-aminomethyl sulfonic acid.—As in the preceding case, methylene-*o*-anisidine sodium bisulfite yielded a disodium salt which was dissolved in a small volume of water and treated cautiously with somewhat more than an equal volume of alcohol. On standing in the cold, the salt separated as orange-red, microscopic needles dissolving readily in water with a deep orange-red color.

*Analyses.* Calc. for  $C_{14}H_{14}O_7N_3SAsNa_2 \cdot 3H_2O$ :  $H_2O$ , 9.95. Found: 9.96.

Calc. for  $C_{14}H_{14}O_7N_3SAsNa_2$ : As, 15.32. Found: 15.52.

In 50% alcohol, mineral acid causes the free arsonic acid to separate as lustrous, flat, violet needles. The anhydrous acid reddens and softens above 155°, and melts with slow gas evolution at 158–60°, dissolving in conc. sulfuric acid with a deep purple color which changes to deep red on standing.

*Analyses.* Calc. for  $C_{14}H_{16}O_7N_3As \cdot 1.5H_2O$ :  $H_2O$ , 5.72. Found: 4.95.

Calc. for  $C_{14}H_{16}O_7N_3As$ : N, 9.44. Found: 9.28.

### (E) Dyes Derived from Arsanilic Acid and Substituted Phenoxyacetic Acids.

**3 - Amino - 6 - [phenyl - (4'-arsonic acid) azo] - phenoxyacetic acid**,  $H_2O_2AsC_6H_4N:NC_6H_3(NH_2)OCH_2CO_2H$ .—*m*-Amino-phenoxyacetic acid<sup>6</sup> yielded a deep red solution which was gently warmed and treated with alcohol, depositing the orange microcrystalline monosodium salt, which was converted into the acid by dissolving in a considerable volume of dilute alcohol with the aid of sodium hydroxide and making the solution just acid to congo red. The acid separated as red, glistening needles. When anhydrous it blackens, but does not melt below 285°, dissolving in conc. sulfuric acid with an orange-red color, in dil. alkalis with an orange color, and gives an orange-red color in 1:1 hydrochloric acid, the hydrochloride separating on rubbing as orange-brown microscopic crystals.

*Analyses.* Calc. for  $C_{14}H_{14}O_6N_3As \cdot 1.5H_2O$ :  $H_2O$ , 6.40. Found: 6.99.

Calc. for  $C_{14}H_{14}O_6N_3As$ : N, 10.63; As, 18.96. Found: N, 10.74; As, 18.75.

**4 - Methyl - 3 - amino - 6 - [phenyl - (4'-arsonic acid) azo] - phenoxyacetic acid**.—4-Methyl-5-amino phenoxyacetic acid<sup>7</sup> gave the monosodium salt of the dye as a red, crystalline mass which was converted as usual into the acid, this separating as dark red aggregates of flat needles with a purple reflex. When rapidly heated to 240°, then slowly, the dye intumesces at 242–3°, with preliminary blackening. It gives an orange color in conc. sulfuric acid or dil. alkalis, and is difficultly soluble in conc. hydrochloric acid, changing on rubbing to an orange-red, microcrystalline hydrochloride.

*Analyses.* Calc. for  $C_{15}H_{16}O_6N_3As \cdot H_2O$ :  $H_2O$ , 4.22. Found: 3.47.

Calc. for  $C_{15}H_{16}O_6N_3As$ : N, 10.27; As, 18.31. Found: N, 10.06; As, 18.51.

**2 - Methyl - 5 - amino - 4 - [phenyl - (4'-arsonic acid) azo] - phenoxyacetic acid**.—In the case of 2-methyl-5-amino-phenoxyacetic acid,<sup>7</sup> the deep red-brown solution of the monosodium salt was filtered, concentrated partially *in vacuo*, and allowed to stand in the cold. The resulting crystals were dissolved in boiling 85% alcohol containing acetic acid, and on cooling the free acid separated. Reprecipitated in 33% alcohol it forms flat, glistening, purplish-brown needles which dissolve readily in methyl alcohol, less easily in ethyl alcohol. When rapidly heated to 185°, then slowly, it intumesces at 187–8°. It dissolves in conc. sulfuric acid with a deep orange color and partially in conc. hydrochloric acid with a red shade, soon depositing the hydrochloride as dull red microcrystals.

*Analyses.* Calc. for  $C_{15}H_{16}O_6N_3As \cdot 2H_2O$ :  $H_2O$ , 8.09. Found: 7.07.

Calc. for  $C_{15}H_{16}O_6N_3As$ : N, 10.27. Found: 10.38.

**3 - Amino - 6 - methoxy - 4 - [phenyl - (4'-arsonic acid) azo] - phenoxyacetic acid**.—Precipitation of the dye acid obtained from 3-amino-6-methoxy-phenoxyacetic acid<sup>8</sup> was facilitated by the addition of acetic acid and the collected product was dissolved in dil. sodium hydroxide, filtered, and reprecipitated with an excess of acetic acid. Reprecipitated in 50% alcohol, the acid separates as flat, glistening, bronze needles and platelets. The air dry acid sinters, softens, and swells at 175–85°, while the anhydrous substance intumesces at 208–13° with preliminary sintering and softening. It dissolves

<sup>6</sup> THIS JOURNAL, 39, 2912 (1917).

<sup>7</sup> *Ibid.*, 39, 2193 (1917).

<sup>8</sup> *Loc. cit.*, p. 2194.

appreciably in the cold in methyl or ethyl alcohol, readily on warming, and dissolves in dil. alkalis or carbonates with an orange-red color. It gives a bright red color in conc. sulfuric acid and yields a deep purplish-red solution in 1:1 hydrochloric acid, almost immediately depositing the hydrochloride as dark brown, microscopic platelets.

*Analyses.* Calc. for  $C_{15}H_{16}O_7N_3As \cdot 4.5H_2O$ :  $H_2O$ , 16.02. Found: 15.47.

Calc. for  $C_{15}H_{16}O_7N_3As$ : N, 9.88. As, 17.64. Found: N, 9.89; As, 17.62.

**4 - Amino - 6 - methoxy - 3 - [phenyl - (4' - arsonic acid) azo] - phenoxyacetic acid.**—Using 4-amino-6-methoxy-phenoxyacetic acid,<sup>9</sup> the monosodium salt of the dye gradually separated, best on concentrating to smaller bulk *in vacuo* and allowing to stand in the ice box. Recrystallized from dil. sodium acetate solution, it separates as chocolate colored, microscopic needles which are very sparingly soluble in water, but dissolve on adding carbonate or alkali with a dark red color.

*Analyses.* Calc. for  $C_{16}H_{18}O_7N_3AsNa \cdot 6H_2O$ :  $H_2O$ , 20.75. Found: 21.03.

Calc. for  $C_{16}H_{18}O_7N_3AsNa$ : As, 16.77. Found: 16.31.

The free acid can be precipitated in 50% alcohol as minute, glistening, maroon platelets. It does not melt below  $280^\circ$ , and dissolves in conc. sulfuric acid with a bright red color. A solution in hot 1:1 hydrochloric acid deposits the hydrochloride on cooling as dark red, flat needles.

*Analyses.* Calc. for  $C_{16}H_{18}O_7N_3As \cdot 2H_2O$ :  $H_2O$ , 7.81. Found: 7.89.

Calc. for  $C_{16}H_{18}O_7N_3As$ : N, 9.89. Found: 9.97.

**4 - Amino - 5 - [phenyl - (4' - arsonic acid) azo] - 1,2-bis-phenoxyacetic acid.**—A  $\rightarrow$  B, using 4-amino-1,2-bis-phenoxyacetic acid.<sup>10</sup> After acidifying with acetic acid the monosodium salt of the dye separated as dark purplish-brown, microcrystalline spherules. It is very sparingly soluble in water, but dissolves with an orange-red color on adding carbonate or alkali.

*Analyses.* Calc. for  $C_{16}H_{18}O_9N_3AsNa \cdot 4.5H_2O$ :  $H_2O$ , 14.17. Found: 14.40.

Calc. for  $C_{16}H_{18}O_9N_3AsNa$ : N, 8.56. Found: 8.61.

When precipitated in much warm 50% alcohol, deposition of amorphous material is prevented and the free acid separates as dark purplish-brown microcrystals. Its repetition of this process was necessary before the acid was analytically pure. A dissolves in conc. sulfuric acid with an orange-red color, and when anhydrous, softens and sinters when heated, but does not melt below  $280^\circ$ .

*Analyses.* Calc. for  $C_{16}H_{18}O_9N_3As \cdot 3H_2O$ :  $H_2O$ , 10.33. Found: 10.58.

Calc. for  $C_{16}H_{18}O_9N_3As$ : N, 8.96. As, 15.97. Found: N, 9.07; As, 15.8.

**$\alpha$  - Amino -  $\beta$  - [phenyl - (4-arsonic acid)] azo -  $\alpha'$  - naphthoxyacetic acid.**— $\alpha$ -Amino- $\alpha'$ -naphthoxyacetic acid<sup>11</sup> gave a deep purple, amorphous precipitate which was dissolved by adding 1 mol. of sodium hydroxide and the solution treated with several volumes of alcohol, causing deposition of the disodium salt. Recrystallized from 50% alcohol, it separates as dark brown, felted microscopic needles which dissolve readily in water with a dark purplish-red color.

*Analyses.* Calc. for  $C_{18}H_{14}O_6N_2AsNa_2 \cdot 9H_2O$ :  $H_2O$ , 24.89. Found: 25.25.

Calc. for  $C_{18}H_{14}O_6N_2AsNa_2$ : N, 8.59; As, 15.33. Found: N, 8.46; As, 15.71.

The free acid may be precipitated in much warm 50% alcohol as flat, dark red needles with a golden luster. It decomposes at about  $285^\circ$ , with preliminary darkening and softening. It dissolves in conc. sulfuric acid with a deep purplish-red color.

*Analysis.* Calc. for  $C_{18}H_{16}O_6N_2As$ : N, 9.44. Found: 9.47.

**$\alpha$  - Amino -  $\alpha'$  - [phenyl - (4-arsonic acid)] azo -  $\beta$  - naphthoxyacetic acid.**—Sodium salt of  $\alpha$ -amino- $\beta$ -naphthoxyacetic acid  $\rightarrow$  neutralized A. The deep purple solution was concentrated to small bulk *in vacuo* and treated with several volumes of alcohol.

<sup>9</sup> *Loc. cit.*, p. 2212.

<sup>10</sup> *Ibid.*, p. 2216.

<sup>11</sup> *Ibid.*, p. 2217.

the disodium salt separating in the cold. Recrystallized from 50% alcohol it forms almost black aggregates of microscopic hairs with a greenish reflex and dissolving in water with a deep red color.

*Analyses.* Calc. for  $C_{13}H_{14}O_6N_3AsNa_2 \cdot 8.5H_2O$ :  $H_2O$ , 23.84. Found: 23.64.

Calc. for  $C_{13}H_{14}O_6N_3AsNa_2$ : N, 8.59; As, 15.33. Found: N, 8.56; As, 15.81.

The free acid, when liberated in much 50% alcohol slowly separates as red-brown microcrystalline aggregates which do not melt below  $285^\circ$ .

*Analyses.* Calc. for  $C_{13}H_{16}O_6N_3As \cdot H_2O$ :  $H_2O$ , 3.89. Found: 3.96.

Calc. for  $C_{13}H_{16}O_6N_3As$ : N, 9.44. Found: 9.49.

2 - Hydroxy - 5 - [phenyl - (4'-arsonic acid) azo] - phenoxyacetic acid.—Neutral A  $\rightarrow$  alkaline *o*-hydroxy-phenoxyacetic acid solution. The neutralized solution was concentrated to small bulk *in vacuo*, and the dye precipitated by adding strong sodium hydroxide solution. Dissolved in hot 50% alcohol and treated with an excess of acetic acid, the monosodium salt separated as yellow, indefinitely crystalline, microscopic globules.

*Analyses.* Calc. for  $C_{14}H_{12}O_7N_2AsNa$ : N, 6.70; As, 17.93. Found: N, 6.42; As, 18.33.

The free arsonic acid separated from a solution in dil. sodium hydroxide as an emulsion which soon crystallized. Dissolved in boiling 85% alcohol, and the filtrate diluted with water, the acid separated as brown, microscopic platelets which do not melt below  $280^\circ$ . It dissolves in boiling alcohol, and gives a bright orange solution in dil. sodium hydroxide. The color in conc. sulfuric acid is a deep red-orange.

*Analyses.* Calc. for  $C_{14}H_{12}O_7N_2As \cdot 0.5H_2O$ :  $H_2O$ , 2.2. Found: 2.4.

Calc. for  $C_{14}H_{12}O_7N_2As$ : N, 7.07; As, 18.92. Found: N, 6.99; As, 18.61.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY. No. 7.]

## CHROMO-ISOMERIC SILVER SALTS OF PENTABROMOPHENOL AND A THEORY OF CHROMO-ISOMERISM OF SOLID COMPOUNDS.

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Received March 4, 1921.

### 1. Previous Investigations.

Two silver salts of pentabromophenol have been described. Bodroux<sup>1</sup> obtained a rose-colored amorphous precipitate upon adding silver nitrate to a solution of the potassium salt. Hantzsch and Scholtze<sup>2</sup> also obtained a reddish amorphous precipitate in the same manner, ascribing the color to an impurity present in the pentabromophenol; but they also described a colorless, amorphous form, which precipitates when alcoholic silver nitrate is added to an alcoholic solution of the ammonium salt, and they apparently regard it as a purer lot of the same salt, which they describe as colorless, and existing in only one form. Isomeric silver salts of other

<sup>1</sup> Bodroux, *Compt. rend.*, 126, 1282-85 (1898).

<sup>2</sup> Hantzsch and Scholtze, *Ber.*, 40, 4882 (1907).



phenols are described by Hantzsch and Scholtze,<sup>2</sup> by Torrey and Hunter,<sup>3</sup> and by Hunter and Joyce.<sup>4</sup>

## 2. Outline of This Investigation.

In the work described in this article, in order to eliminate the possibility of the color being due to impurities, the pentabromophenol was carefully purified by repeated crystallizations from alcohol and by boiling with animal charcoal until a colorless product was obtained and the melting point of successive crops did not change.

The determination of silver in the various salts was carried out by the cyanide-sulfide method as described by Lucas and Kemp.<sup>5</sup> The accuracy of this method was demonstrated in the case of the salt of the formula  $C_6Br_5OAg$ , which is stable and can be obtained in a high degree of purity. This salt was prepared by heating the yellow crystalline ammoniate of the formula  $C_6Br_5OAg \cdot 2NH_3$ . The formula  $C_6Br_5OAg$  requires 18.11% of silver. Three analyses gave 18.10%, 18.12%, and 18.12%—results which show that the method is highly accurate.

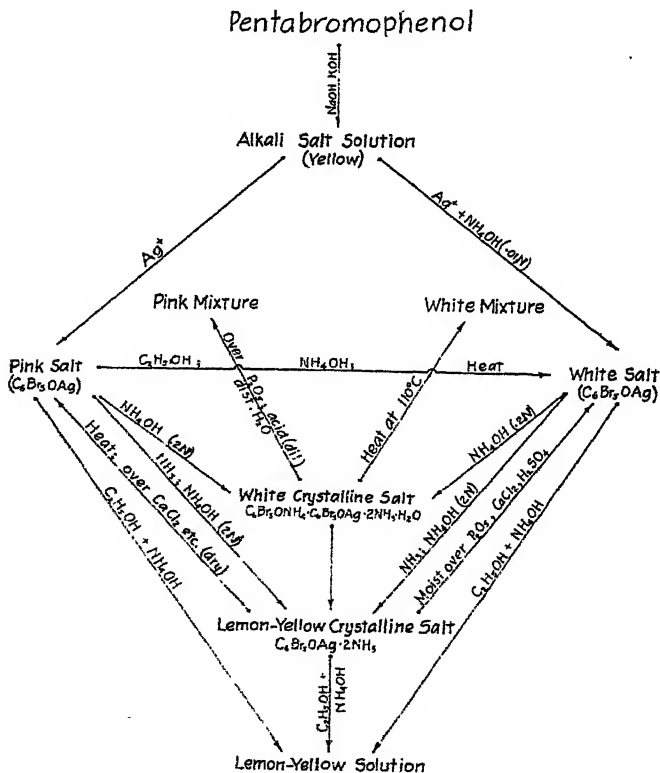


Fig. 1.

<sup>3</sup> Torrey and Hunter, *THIS JOURNAL*, 33, 194-205 (1911); *Ber.*, 40, 4332 (1907).

<sup>4</sup> Hunter and Joyce, *THIS JOURNAL*, 39, 2640 (1917).

<sup>5</sup> Lucas and Kemp, *ibid.*, 39, 2074 (1917).

When pentabromophenol is treated with a solution of sodium hydroxide it dissolves, and the solution has a yellow color. The color is intensified on heating, but fades again on cooling. Diluting the solution causes a gradual fading out of the color. The sodium salt of pentabromophenol crystallizes from this yellow aqueous solution in colorless featherlike needles. The color of the solution is not due to impurities; for it persists after repeated crystallizations of the white pentabromophenol.

The pink silver salt separates when silver nitrate solution is added to the sodium pentabromophenolate solution; but, if the silver nitrate is 0.01 *N* in ammonium hydroxide, the colorless form precipitates. The concentration of ammonia must not be much greater, because at about 0.2 *N* another salt, consisting of an ammoniate, separates—a colorless shimmering crystalline compound, which has a satiny appearance as it moves through the liquid. If the concentration of ammonia is still greater, another ammoniate which can be obtained in well-defined yellow needles, separates after standing.

The accompanying chart shows the relationships between the phenol, the colored and colorless silver salts, and the two ammoniates.

### 3. Discussion of the Color Relations and a New Theory of Chromoisomerism.

It seems unreasonable to ascribe the color of the solution of the sodium salt to tautomerism of the benzoid-quinoid type, because it must then be assumed that sodium is linked to carbon. Compounds in which sodium is known to be joined to carbon are decomposed by water with formation of sodium hydroxide. Thus the carbides of sodium and potassium<sup>6</sup> react vigorously with water, and so does sodium phenyl,<sup>7</sup> forming sodium hydroxide and benzene. The fact that the colorless salt gives rise to a colored solution must therefore be ascribed either to some other structural change or electronic condition. Now, since in solution the sodium salt is largely ionized, it is clear that the difference in color must be due to some difference in the powers of absorbing light possessed by the ion and by the un-ionized molecule. According to present views, however, the absorption of light is caused by the vibration of electrons, and this must increase with the looseness with which the electrons are bound and with the corresponding tendency of the compound to undergo structural changes or shifting of the valence bonds. Now the production of the anion is accompanied by the formation of a powerful negative electrostatic field, which decreases the effective attraction of the carbon atoms for the electrons; and the latter, being under less restraint, vibrate in

<sup>6</sup> Matignon, *Compt. rend.*, **125**, 1033-5 (1897).

<sup>7</sup> Acree, *Am. Chem. J.*, **29**, 590 (1903).

longer periods. The ion absorbs in the visible violet, and the solution is yellow. This greater vibration may well correspond to an oscillation of the double and single valences between the carbon atoms of the benzene ring. It is known in general that the introduction of halogen into the benzene nucleus causes a shifting of the absorption bands towards the red,<sup>8</sup> and that the addition of a strong base to solutions of phenols also causes a shifting of the absorption bands towards the red.<sup>9</sup>

When an ionized substance passes from solution into the solid state, either of two conditions may result, according to the theory of chromo-isomerism here presented.

(1) As has been shown by the recent X-ray work on the structure of crystals, the atoms or atom-groups that form the ions in solution, such as the sodium and chlorine atoms in sodium chloride, maintain in most crystalline substances their separate identities and probably still carry the same charges that they do in aqueous solution. It is evident, however, that the powerful electrostatic fields which accompany the atoms in the ionized condition will be weaker in the crystalline state; for, instead of existing in the solution more or less independently of other ions, each atom is now surrounded by atoms carrying charges of opposite sign. The intensity of vibration of the electrons will therefore be less and the frequency of vibration shorter, so that the absorption will be displaced toward the violet end of the spectrum, and the crystalline substance may become of a paler red or yellow color than that of its ions in solution, or it may even become colorless.

(2) The compound which first crystallizes from solution may be an unstable form, changing to a more stable form under favorable conditions. Whenever such a transition takes place energy is lost from the system. This means that the rearrangement is due to the tendency of the atoms and atom-groups to assume the position in which the electrostatic fields about them are most completely neutralized. Either the ions may still retain their identities in the more stable packing, or they may become chemically united, in other words as intimately associated as the atoms within the atom-group that constituted the ion in solution. Whatever the actual condition, the weakening of the electrostatic fields strengthens the attraction between atoms and electrons, and the latter now vibrate in still shorter periods, so that absorption of light is displaced farther towards the violet. A solid substance which was still colored in the unstable form, will become less highly colored or even colorless in the stable form; in other words, a change in the electrostatic environment of the absorbing atoms or atom groups brings about

<sup>8</sup> Baly, *J. Chem. Soc.*, 99, 856 (1911); Purvis, *ibid.*, 99, 825 (1911); 107, 966 (1915).

<sup>9</sup> Ewbank, *ibid.*, 87, 1347 (1905); Baly, Tuck and Marsden, *ibid.*, 97, 582 (1910); Wright, *ibid.*, 100, 676 (1900).

a corresponding change in the wave length of the light absorbed, and the wave length is longest when the electrostatic fields are the strongest.

The fact that the solid sodium salt of pentabromophenol is colorless while its anion is yellow may be attributed to either of these conditions. But the existence of two solid silver salts, one of which is pink and the other white, requires for its explanation both assumptions. The facts in regard to these silver salts and their bearing upon this explanation may therefore be more fully considered. They may be briefly summarized as follows.

The analyses of the salts show that they have the same percentage composition. The pink salt is the more reactive. Thus, when the freshly precipitated moist salts are covered with about 20 cc. of alcohol-free ether and 5 cc. of ethyl iodide is added, both give the same product, pentabromophenyl ethyl ether, but the reaction takes place more rapidly with the pink salt. Its color fades slowly, and it is largely changed to silver iodide within one-half hour; whereas the white salt under the same conditions is not completely converted during a much longer time. When put in an atmosphere containing ammonia both salts finally give the same ammonia addition product, but the rate of ammonia absorption by the pink form is more rapid.

All these facts are simply accounted for by the hypothesis that the pink salt is the unstable, more reactive form, and that the white salt is the stable, less reactive form.

That the pink salt is unstable is shown by the ease with which transformation to the colorless form takes place. When the pink form is brought into solution, even to a very slight extent, as may be done by heating it in contact with water or by the addition of a small amount of alcohol or ammonia, the white form results. Thus the color of the pink salt may be ascribed to the same factor as that which gives the color to the solution of the sodium salt, namely, to a strong electrostatic field about the pentabromophenolate ion; while in the white salt the ions have taken up the positions in which their electrostatic fields are most completely neutralized. Thus also the pink salt results when precipitation takes place so rapidly that there is not time for the ions to arrange themselves in the final, more intimate, association characteristic of the more stable white salt.

The color of the yellow ammoniate of silver pentabromophenolate can be readily accounted for on the basis of this theory, since the electrostatic environment is modified by the association of two molecules of the polar compound ammonia with each silver atom, an increase in the strength of the electrostatic fields resulting.

The production of color in the cases mentioned above, *viz.*, the aqueous

solution of the sodium salt, the pink silver salt, and the yellow silver ammoniate, is ascribed to the vibration of the electrons between the carbon atoms of the benzene ring. If such is actually the case, then we should expect visible light to be absorbed by the same mechanism in the case of complex benzene derivatives, particularly when they are in strong electrostatic fields.

The theory that chromo-isomerism in solid salts may arise not only from a difference in molecular structure, but from a difference in crystal structure, when this produces a variation in the strength of the electrostatic field which is associated with the atoms or atom groups of the compound, is applicable to inorganic compounds. For example, the cubic modification of mercuric sulfide is black, the trigonal is red; the cubic modification of thallous iodide is deep red, the rhombic is yellowish-green; the tetragonal modification of mercuric iodide is red, the rhombic is yellow; the trigonal modification of antimony tri-iodide is red, the rhombic is yellowish-green, and the monoclinic is greenish-yellow. It will be noted that the more symmetrical crystal form has the darker color. This seems to justify the conclusion that whenever a compound exists in two or more colored forms, the crystal structure of the darker colored one possesses the greater symmetry. Moreover, the study of crystal structure by means of X-rays indicates that compounds in which the union is entirely polar have the most symmetrical structure and that the presence of more or less firmly bound groups of atoms, *i. e.*, radicals, usually leads to a less symmetrical crystal structure. For example, rock salt crystallizes in the cubic system and calcite in the trigonal. It is probable that greater symmetry goes with a more polar condition, and therefore with greater freedom of vibration owing to the presence of more free charges. It is not surprising, then to find that the deeper colored form of a compound possesses the greater symmetry.

That a difference in crystal structure may account for the different colors of the so-called chromo-isomeric salts of organic acids is shown in the case of thallous picrate. Red thallous picrate is monoclinic, and yellow thallous picrate is triclinic. On the basis of the theory presented, the picrate ion is absorbing light of longer wave length in the former case, because the electrostatic field surrounding it is stronger than in the yellow modification.

When dealing with solutions of colored compounds, it is observed that here also the wave length of the light absorbed varies with the electrostatic environment, in general being greatest in the polar, and least in the non-polar solvents. Thus the head of the absorption band of 4-nitro-*o*-xylene lies closer to the red in alcoholic than in petroleum ether solution, and in the case of nitroquinol dimethyl ether the absorption band progressively shifts to the red in the following solvents in the order

named: light petroleum ether, benzene, alcohol, chloroform, pyridine, water, aniline and conc. sulfuric acid.<sup>10</sup>

Finally, on the basis of this theory, it is not necessary to assume a different structural formula for each differently colored modification of a compound. The whole field of the relationship between color and constitution could be much clarified by applying the principles discussed above.

#### 4. The Experimental Work.

The pentabromophenol used in this work was prepared by the method of Bodroux,<sup>11</sup> which consists in treating phenol with bromine in the presence of anhydrous aluminum bromide. The crude product was treated with cold 95% alcohol to extract the aluminum bromide and lower halogenated products. It was dissolved in hot alcohol, boiled with refined bone charcoal, and allowed to cool slowly, when it crystallized in long needles. This operation was repeated several times, yielding a snow-white product, melting at 229.5° (corr).

The pink silver pentabromophenolate.—A solution of the sodium salt was made by dissolving the phenol in an equivalent quantity of sodium hydroxide in solution which was practically free from chlorides. The solution thus prepared was yellow, and alkaline to litmus. It was diluted until about 0.01 *N*; then a slight excess of 0.05 *N* silver nitrate was added slowly with stirring. The precipitate was brown, due to the presence of silver oxide, but changed to pink on the addition of 0.01 *N* acetic acid until the liquid showed a slight acid reaction with litmus. The precipitate was filtered, the solid removed from the filter and shaken up with much water, filtered again, and after washing thoroughly to remove impurities, sucked as dry as possible. It was placed on a watch glass, allowed to dry for one day in a clean cupboard, then pulverized, spread out thin on a watch glass, and dried over phosphorus pentoxide for several days *in vacuo*. The product was analyzed for silver by the cyanide-sulfide method.<sup>5</sup>

##### ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag <sub>2</sub> S. G.	Ag. found. %.	Ag. calc. from C <sub>6</sub> Br <sub>5</sub> OAg %.
I.....	0.3043	0.0627	17.94	18.11
II.....	0.3475	0.0716	17.94	18.11
III.....	0.4734	0.0975	17.93	18.11

The pink salt was also prepared by heating the yellow ammoniate for several hours at 120°.

##### ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag <sub>2</sub> S. G.	Ag. found. %.	Ag. calc. from C <sub>6</sub> Br <sub>5</sub> OAg %.
I.....	0.3457	0.0781	18.10	18.11
II.....	0.4492	0.0935	18.12	18.11
III.....	0.2806	0.0584	18.12	18.11

When prepared by the latter method it is much purer than by precipitation, because the yellow ammoniate can be obtained very pure.

The pink salt is insoluble in water, alcohol, ether, ligroin, benzene, carbon tetrachloride, bromobenzene, etc. It dissolves in alcohol to which a little ammonium hydroxide has been added, yielding a deep lemon-yellow solution. With ethyl iodide the dry salt

<sup>10</sup> Baly, Tuck and Marsden, *loc. cit.*; Baly and Rice, *J. Chem. Soc.*, 101, 1478 (1912).

<sup>11</sup> Bodroux, *Compt. rend.*, 126, 1282-5 (1898).

seems to decompose in a manner analogous to the catalytic decomposition first observed by Torrey and Hunter<sup>3</sup> in the case of silver tribromophenolate, and later studied by other investigators.<sup>12</sup> The insoluble pink silver pentabromophenolate first becomes green, then black, and finally yellow; the liquid is not colored during the course of the reaction. No effort was made to study this reaction further. When the moist freshly precipitated salt is covered with about 20 cc. of ether and 4 to 5 cc. of ethyl iodide, the pink color slowly fades until after about one-half hour the solid appears to be entirely silver iodide. If the ether layer is filtered, the solid thoroughly extracted with ether and the solvent allowed to evaporate, pentabromophenyl ethyl ether separates in long slender needles, melting<sup>13</sup> at 131° to 134° (corr.), and after one crystallization from alcohol at 134° to 135° (cor.). From 1.3 g. of the phenol there was obtained 1.1 g. of the ether, a yield of 80%.

The moist pink silver salt is converted into the more stable colorless form on heating, also in the presence of a small amount of alcohol or ammonia. If treated with stronger aqueous ammonia the white ammoniate forms, which goes over into the yellow ammoniate when warmed with strong ammonia solutions. These transformations can be carried out either in the presence or absence of excess silver ion.

**The White Silver Pentabromophenolate.**—This may be prepared from the pink salt, as described above, or directly by the addition of 0.05 *N* silver nitrate solution to the 0.01 *N* solution of the sodium salt made 0.01 *N* with respect to ammonia. The product after washing and drying is a very light cream color.

Sample.	ANALYSES.			
	Wt. of sample. G.	Wt. of Ag <sub>2</sub> S. G.	Ag. found. %.	Ag. calc. from C <sub>5</sub> Br <sub>5</sub> OH. %.
I.....	0.3918	0.0807	17.93	18.11
II.....	0.4131	0.0851	17.93	18.11
III.....	0.4701	0.0965	17.88	18.11
IV.....	0.2544	0.0523	17.91	18.11
V.....	0.2118	0.0439	18.06	18.11

The white salt closely resembles the pink in being insoluble in the solvents named above, and dissolving in alcohol containing ammonium hydroxide to form a lemon-yellow solution. It also decomposes with dry ethyl iodide. The moist salt reacts slowly with a solution of ethyl iodide in ether to form the pentabromophenyl ethyl ether. The freshly precipitated white silver salt from 1.8 g. of pentabromophenol was covered with a solution of ethyl iodide in ether, but the rate of reaction was so slow that there was no noticeable change in the color of the solid during an hour, in marked contrast to the more rapid reaction of the pink salt. After standing for 12 hours, there was obtained 1.4 g. of white solid melting at 132–4° (corr.), which was recrystallized from alcohol in the form of long, slender needles that melted at 134–5° (corr.). The yield of pentabromophenyl ethyl ether was about 70%.

In contact with ammonium hydroxide of about 0.2 *N* the silver salt goes over into the white crystalline ammoniate, which dissolves in more concentrated ammonia on heating. From this solution the yellow ammoniate crystallizes if the dilution is not too great.

**The White Crystalline Ammoniate.**—This is formed from either the pink or white salt, as described above, or directly from silver nitrate and the sodium salt, if the concentration of ammonia in the solution is 0.2 *N* or greater. It has a beautiful satiny appearance, reflecting light much as does precipitated mercurous chloride. Under the

<sup>12</sup> Hunter, Olson and Daniels, *THIS JOURNAL*, 38, 1761–71 (1916); Woollett, *ibid.*, 38, 2474–8 (1916).

<sup>13</sup> Bonneaud, *Bull. soc. chim.*, 7, 776–81 (1910), gives 136° for the melting point.

microscope the small particles appear as very thin plates, which revolve rapidly as they migrate through the solution.

The salt was filtered and washed with dil. ammonium hydroxide and dried in desiccators containing a small amount of ammonia, one desiccator having sodium hydroxide, and another a mixture of hydrated and anhydrous sodium sulfate as drying agents. That the moist solid has an appreciable vapor pressure of ammonia is shown by the fact that when washed with water or dil. acids, or when dried over phosphorus pentoxide *in vacuo* it turns pink. The dried products from both desiccators retained their crystalline appearance, and were apparently stable upon exposure to air. Analysis for silver and for bromine (by Carius' method) gave the following results, which show the presence of 10 atoms of bromine to one of silver.

Instead of determining the silver bromide, which was mixed with broken glass, the silver contained in it was determined by the cyanide-sulfide method, and the percentage of bromine calculated from the weight of silver sulfide.

## ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag <sub>2</sub> S. G.	Ag. found. %.	Ag. calc. from C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> N <sub>3</sub> Br <sub>10</sub> Ag. %.
I.....	0.5913	0.0637	9.38	9.35
II.....	0.5760	0.0621	9.39	9.35
III.....	0.7476	0.0796	9.27	9.35
IV.....	0.3474	0.0374	9.37	9.35
V.....	0.3203	0.0342	9.30	9.35

I, II and III were dried over sodium sulfate, IV and V were dried over sodium hydroxide.

## ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag <sub>2</sub> S. G.	Br. found. %.	Br. calc. from C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> N <sub>3</sub> Br <sub>10</sub> Ag. %.
I.....	0.1720	0.1834	68.76	69.31
II.....	0.1970	0.2100	68.74	69.31

Nitrogen was determined by the method of Kjeldahl, with the following results, which indicate 3 atoms of nitrogen to 1 of silver.

## ANALYSES.

Sample.	Wt. of sample. G.	HCl (0.4942N) used. Cc.	N found. %.	N calc. from C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> N <sub>3</sub> Br <sub>10</sub> Ag. %.
I.....	1.065	5.32	3.46	3.64
II.....	1.319	6.90	3.62	3.64

Loss on heating was determined by heating 0.6825 g. of the salt dried over sodium hydroxide at 120° to constant weight of 0.6395 g. The loss was 0.0430 g., or 6.30%. Calculated as 3 molecules of ammonia and 1 molecule of water from C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>3</sub>Br<sub>10</sub>Ag, the calculated loss is 5.98.

Some of the pink product obtained by drying the white ammoniate over phosphorus pentoxide was analyzed for silver.

## ANALYSES.

Sample.	Wt. of sample. G.	Wt. of Ag <sub>2</sub> S. G.	Ag. found. %.	Ag. calc. from C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> Br <sub>10</sub> Ag. %.
I.....	0.3515	0.0401	9.93	9.95
II.....	0.2938	0.0335	9.93	9.95

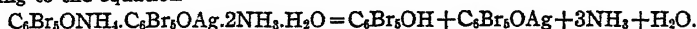
These results indicate that 3 molecules of ammonia and 1 of water were lost from C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>3</sub>Br<sub>10</sub>Ag.



Ammonium pentabromophenolate is stable over phosphorus pentoxide and when heated to 110° loses ammonia to give a snow-white residue of the pure phenol.

When boiled with alcohol the white crystalline salt leaves a residue of white silver pentabromophenolate and a filtrate containing pentabromophenol in solution, the two approximately equal in amount. If dilute sodium hydroxide is used the same decomposition is observed, except that the phenol is now dissolved as the sodium salt.

From the above data it appears that the white crystalline ammoniate is a double salt of the formula  $C_6Br_5ONH_4.C_6Br_5OAg.2NH_3.H_2O$ , and that it is easily decomposed according to the equation



The silver salt resulting from this decomposition is pink or white, depending upon the conditions.

**The Lemon-yellow Ammoniate of Silver Pentabromophenolate.**—This may be obtained from the salts already described, but is best prepared directly from the solution of the sodium salt by first making it 2 *N* in ammonia and then adding an excess of silver nitrate. The white crystalline salt which first separates is dissolved by warming the solution, which is filtered and the filtrate allowed to stand several hours, when long lemon-yellow needles crystallize. They are filtered with suction, washed in strong ammonia solution, and dried over sodium hydroxide in a desiccator containing a little ammonium chloride. The crystals upon drying retain their color and crystalline structure. The dry salt loses ammonia very slowly at ordinary temperatures, but when heated at 100° to 110° the decomposition is rapid and the pink form of the silver salt remains. This is a deeper red than when formed by precipitation. The yellow salt dissolves in alcohol containing ammonia to give the characteristic lemon-yellow solution (see Fig. 1).

Sample.	ANALYSES.			
	Wt. of sample. G.	Wt. of Ag <sub>2</sub> S. G.	2Ag. found. %.	Ag. calc. from $C_6Br_5OAg.2NH_3$ . %.
I.....	0.2907	0.0570	17.07	17.10
II.....	0.2715	0.0532	17.06	17.10
III.....	0.2470	0.0487	17.17	17.10

When 1.249 g. was heated at 110° to constant weight it lost 0.0684 g., corresponding to 5.46%; the percentage of ammonia calculated from  $C_6Br_5OAg.2NH_3$  is 5.40.

**Absorption of Ammonia by Silver Pentabromophenolate.**—Under the proper conditions the two forms of this salt absorb ammonia to form the yellow ammoniate. But when the vapor pressure of ammonia above the salts is low, only partial absorption takes place, and at different rates for the two salts. Samples of the two salts were weighed out on watch glasses and placed in the same desiccator containing sodium hydroxide and a small amount of ammonium chloride. The salts were taken out at intervals and weighed.

Time elapsed. hours.	Percentage of $NH_3$ .	
	Pink salt. %.	White salt. %.
3	4.96	0.70
6.5	4.96	0.88
22	4.96	1.29
27.5	4.96	1.29

After the salts would no longer absorb ammonia at room temperature, the desiccator was placed in an ice-chest beside the ice. After remaining for 3 hours the salts were again weighed but no change was found. The salts were then transferred to a desiccator containing a much higher partial pressure of ammonia and allowed to stand for 36 hours at room temperature with the result that the percentage of ammonia in the

pink salt increased from 4.96 to the theoretical percentage (5.40%) while that in the white increased from 1.29% to 5.01%. After standing for 4 days in the same desiccator, the percentage of ammonia in the white increased to 5.09%.

The above data show that the absorption of ammonia by the white salt is very much slower than by the pink form. This cannot be due to a difference in the physical state, as the white salt was light and fluffy while the pink was very compact. The total absorption of ammonia by both salts seems to depend upon the partial pressure of the ammonia in the desiccator.

**Other Salts of Pentabromophenol.**—Various salts were prepared by adding neutral solutions of metallic salts to a dilute solution of the sodium salt of pentabromophenol. The following is a list of the positive ions which form difficultly soluble salts with pentabromophenol.

Salts. Colored, not distinctly crystalline.		Salts. White, not distinctly crystalline.		White crystalline salts.	
Ions.	Color.	Ions.		Ions.	
$\text{Cu}^+$	light brown	$\text{Ba}^{++}$		$\text{K}^+$	
$\text{Cu}^{++a}$	red	$\text{Cd}^{++}$		$\text{NH}_4^+$	
$\text{Co}^{++}$	light pink	$\text{Ca}^{++}$		$\text{Li}^+$	
$\text{Fe}^{+++}$	brown	$\text{Ni}^{++d}$		$\text{Mg}^{++}$	
$\text{Fe}^{++}$	yellow	$\text{Mn}^{++}$		....	
$\text{Pb}^{++}$	light yellow	$\text{Zn}^{++}$		....	
$\text{Hg}^{+b}$	orange	$\text{Tl}^+$		....	
$\text{Hg}^{++}$	yellow	....		....	

<sup>a</sup> Dissolves in warm 6 *N* ammonium hydroxide which, upon cooling, deposits dark brown needles.

<sup>b</sup> Changes to a perfectly colorless salt upon standing exposed to sunlight.

<sup>c</sup> Changes to a deep violet salt upon standing exposed to sunlight. The violet precipitate dissolves in warm 6 *N* ammonium hydroxide from which lemon-yellow needles separate upon cooling.

<sup>d</sup> Dissolves in warm 6 *N* ammonium hydroxide from which light green needles deposit upon cooling.

## 5. Summary.

1. The silver salt of pentabromophenol exists in two forms, one pink, the other colorless; and in both forms silver is joined to oxygen.

2. Two ammoniates of silver pentabromophenolate are described, one a yellow salt,  $\text{C}_{65}\text{BrOAg} \cdot 2\text{NH}_3$ , and the other a double salt of the formula  $\text{C}_6\text{Br}_5\text{ONH}_4 \cdot \text{C}_6\text{Br}_5\text{OAg} \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ .

3. A new theory of chromo-isomerism is proposed, on the basis of which the wave length of the light absorbed by a substance will change as the electrostatic environment of the absorbing atoms or atom-groups changes, and will be longest when the electrostatic fields are the strongest.

4. The theory satisfactorily accounts for the yellow color of aqueous solutions of the colorless sodium pentabromophenolate, for the color of the two forms of the silver salt, and for the yellow color of the ammonia addition compound of the latter.

5. Absorption of light in these cases is ascribed to the isorropesis of the benzene ring. It is undoubtedly a factor in color production in the case of other benzene derivatives.

6. The theory satisfactorily accounts for the different colors of polymorphic forms of inorganic compounds, such as mercuric iodide, thallos iodide, etc. The more symmetrical form is the darker colored, because the electrostatic fields about the atoms are stronger in the more symmetrical forms.

7. According to the theory presented, it is not necessary to assign a different formula to each colored modification of a compound. The entire field of color and constitution should be re-examined on the basis of this theory.

In conclusion, the assistance and valuable criticism of Dr. Arthur A. Noyes and Dr. Roscoe G. Dickinson in connection with the development of the theory are gratefully acknowledged.

PASADENA, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

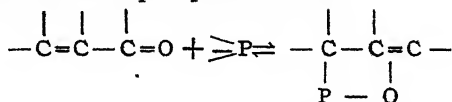
## ADDITION REACTIONS OF PHOSPHORUS HALIDES. II. THE 1,4-ADDITION OF PHOSPHENYL CHLORIDE.

BY JAMES B. CONANT AND S. M. POLLACK.

Received March 17, 1921.

### I. Introduction.

Phosphorus trichloride readily combines with the carbonyl group of aldehydes<sup>1</sup> and with the conjugated system of  $\alpha,\beta$  unsaturated ketones.<sup>2</sup> This combination involves the formation of a ring containing as one of its members a pentavalent phosphorus atom.



The reaction is reversible and the product cannot be isolated, but may be transformed by suitable reagents into a stable phosphonic acid or its derivative.

These addition reactions are analogous to the formation of the pentahalides by the addition of chlorine or bromine to phosphorus trichloride. The trivalent phosphorus atom is unsaturated, as shown by its combination with the halogens, the carbonyl group or the ends of a conjugated system in unsaturated ketones. The organic derivatives of phosphorus trichloride (the chloro-phosphines) are also unsaturated since they readily unite with two atoms of chlorine. It is, therefore, to be expected that they will combine with certain unsaturated organic substances in a manner completely parallel to phosphorus trichloride itself. Michaelis, in fact, in his exhaustive study of these compounds showed<sup>3</sup> that benzaldehyde combined

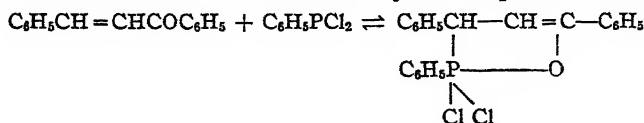
<sup>1</sup> THIS JOURNAL, 42, 2337 (1920).

<sup>2</sup> *Ibid.*, 39, 2679 (1917); 42, 830 (1920).

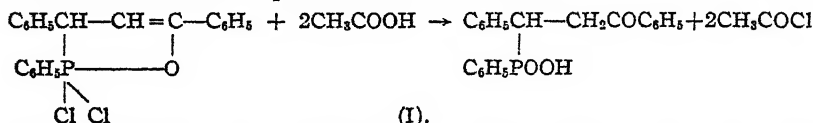
<sup>3</sup> Michaelis, *Ann.*, 293, 193 (1896).

with dichloro-phenylphosphine (phosphenyl chloride) and he was able to isolate a phosphonic acid by treatment of the addition product with water. This is obviously a case of addition to the carbonyl group.

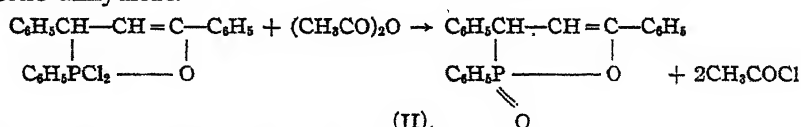
The results here presented show that phosphenyl chloride combines with the ends of the conjugated system of benzal-acetophenone. As in the case of the trichloride an intermediate cyclic compound is first formed.



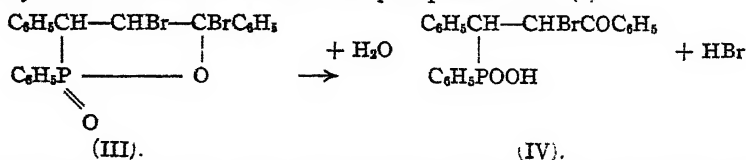
This readily reacts with acetic acid producing acetyl chloride and a keto-phosphonic acid (I). The chlorine atoms of the addition compound, like those of  $\text{C}_6\text{H}_5\text{PCl}_4$ , are more reactive than those in phosphenyl chloride. As a result phosphenyl chloride and benzal-acetophenone, when mixed with acetic acid, form the keto-phosphonic acid almost quantitatively; the equilibrium of the primary reversible reaction is shifted by the rapid reaction of the addition product with acetic acid.



The proof of the structure of the intermediate cyclic compound rests on the structure of a cyclic anhydride (II) obtained by the action of acetic anhydride. Here again the addition product is more reactive than phosphenyl chloride and the reaction goes to completion in the presence of acetic anhydride.



The cyclic anhydride (II) could be isolated only as an impure gum, but its structure is clearly established by its reactions. On treatment with water it yields the phosphonic acid (I). It combines with two atoms of bromine, thus showing that it is unsaturated. The resulting dibromide (III) on treatment with water forms hydrobromic acid and two isomeric  $\beta$ -bromoketo-phosphonic acids (IV) which are identical with the substances made by the bromination of the keto-phosphonic acid (I).

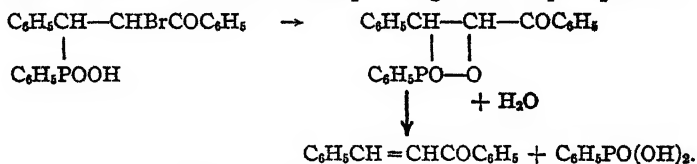


The bromo acid contains two asymmetric carbon atoms, and thus two

racemic stereo-isomers are possible; both were formed by the bromination of the keto-phosphonic acid, and also by the action of water on the cyclic dibromide. This evidence seems to establish clearly the structure of the anhydride and in turn that of the addition product. Thus, the phosphorus atom in phosphenyl chloride like that in the trichloride,<sup>2</sup> adds to the 1,4 position of the conjugated system.

The two isomeric bromine compounds are stereo-isomers and not structural isomers since they are both decomposed by alkaline reagents with the formation of benzal-acetophenone. This reaction is parallel to the behavior of the  $\beta$ -bromo acid previously studied<sup>2</sup> and establishes the fact that the bromine atom is in the  $\beta$  position. The low-melting isomer may be transformed into the high-melting one by the prolonged action of sunlight on its chloroform solution.

It is interesting to note that the two isomers decompose in aqueous sodium carbonate at appreciably different rates, and both seem to be somewhat more stable in this regard than the  $\beta$ -bromo acid obtained in the work with phosphorus trichloride. It seems possible that this reaction may involve the intermediate formation of a  $\beta$ -phostone (analogous to a  $\beta$ -lactone) which then easily decomposes in the presence of water to form the unsaturated ketone, and the corresponding acid of phosphorus.



Many  $\beta$ -lactones easily lose carbon dioxide with the production of unsaturated compounds, which is a reaction analogous to that shown above.

## II. Experimental.

$\alpha$ -Phenyl- $\beta$ -benzoyl-ethyl-phenylphosphonic Acid,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5\text{POOH})\text{CH}_2\text{CO}-\text{C}_6\text{H}_5$ .—Ten g. of benzal-acetophenone was dissolved in a mixture of 9 g. of phosphenyl chloride and 15 g. of glacial acetic acid. The ketone went quickly into solution, which in the course of a few minutes began to become warm and deposit a white crystalline material; the presence of acetyl chloride could be recognized by its odor. The mixture was cooled with running water and after considerable solid had separated 70 cc. of glacial acetic acid was added with stirring. At the end of 30 minutes the mixture was poured into water and the solid filtered off, washed with ethyl alcohol and dried. 19 g. was thus obtained; this is slightly more than the calculated amount. The crude product thus obtained can be best purified by dissolving in sodium carbonate, extracting with ether and reprecipitating with acid. It is very insoluble in all solvents but may be recrystallized from its very dilute solutions in hot glacial acetic acid or ethyl alcohol. It melts with decomposition at  $220^\circ$  to  $225^\circ$ .

*Analysis.* Calc. for  $\text{C}_{21}\text{H}_{19}\text{O}_3\text{P}$ : P, 8.9. Found: 8.7.

Titration with standard sodium hydroxide solution using phenolphthalein as an indicator, showed the compound to be a monobasic acid.

$\alpha$ -Phenyl- $\beta$ -bromo- $\beta$ -benzoyl-ethyl-phenylphosphonic Acid,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5\text{POOH})-$

$\text{CHBrCOC}_6\text{H}_5$ .—The phosphonic acid was so insoluble that it could be brominated only in glacial acetic acid. Five g. of the crude acid was brominated with 2.7 g. of bromine by the following procedure. The acid was suspended in 20 cc. of glacial acetic acid and the mixture heated to the boiling point. A small portion of the bromine was added and the heating continued until the color disappeared (about 5 minutes). The bromine was then added slowly and the temperature kept a little below the boiling point of the acetic acid. The reaction proceeded rapidly after it had once started and hydrogen bromide was given off freely. The solid went into solution as the reaction continued, and at the end a clear colorless solution resulted. This was poured into 500 cc. of water, and the solid filtered off and dried. It weighed 6.5 g. and had a melting point of  $160^\circ$  to  $180^\circ$ . This mixture of stereo-isomeric bromine compounds could be separated only with difficulty, as much decomposition took place on heating them in any solvent, particularly methyl and ethyl alcohols. The separation was best effected by treating with 50 cc. of hot chloroform, filtering off the insoluble compound and evaporating the chloroform solution to a volume of 20 cc. On the addition of petroleum ether the low-melting isomer slowly crystallized. 2 g. of substance melting at  $150^\circ$  was thus obtained. The insoluble material was recrystallized from ethyl alcohol; 1 g. of substance melting at  $195^\circ$  was obtained. Recrystallization from the same solvent did not change the melting point.

*High-melting isomer*.—This substance melted with decomposition at  $195^\circ$ . It is very insoluble in all solvents.

*Analysis*. Calc. for  $\text{C}_{21}\text{H}_{18}\text{O}_3\text{PBr}$ : Br, 18.7. Found: 18.6.

*Low-melting isomer*.—This substance melted at  $150^\circ$ ; it is fairly soluble in methyl and ethyl alcohols and very soluble in chloroform. It is only sparingly soluble in petroleum ether.

*Analysis*. Calc. for  $\text{C}_{22}\text{H}_{18}\text{O}_4\text{PBr}$ : Br, 18.7. Found: 19.1.

Both isomers dissolve in aqueous sodium carbonate—although the high-melting isomer only slowly (probably because of its extreme insolubility). When treated with sodium hydroxide solution both substances dissolve and are almost immediately decomposed with the formation of benzal-acetophenone which separates as a precipitate. This same decomposition takes place more slowly in sodium carbonate solution. A dilute sodium carbonate solution of the low-melting isomer became milky after standing for 5 minutes at room temperature. In a parallel experiment with the high-melting substance the solution reached the same degree of opalescence after standing for about 40 minutes. An increase in temperature greatly facilitates this decomposition.

A chloroform solution of the isomer melting at  $149^\circ$  was made faintly red with a trace of iodine and exposed to sunlight. The high-melting isomer very slowly separated, and after many weeks over half of the material had been transformed. The product was identified by a mixed-melting-point determination with the pure substance melting at  $195^\circ$ .

### Reaction in Acetic Anhydride.

The reaction between benzal-acetophenone, phosphenyl chloride, and acetic anhydride is much slower than the corresponding reaction with acetic acid. After evaporating the acetyl chloride formed, the reaction product is left as a gum which is soluble in chloroform. All attempts to obtain a solid substance failed. The reactions of the material, however, show that an unsaturated cyclic anhydride is present at this point. The transformations may be carried out with a chloroform solution of the gum, or with the original reaction mixture somewhat diluted with more acetic anhydride. A typical experiment with each procedure is as follows.

(a) Five g. of benzal-acetophenone, 3.8 g. of acetic anhydride and 4.5 g. of phosphenyl chloride were mixed and allowed to stand for one hour at room temperature and then for 3 hours at 40°. The acetyl chloride and excess of acetic anhydride were evaporated under diminished pressure at a temperature of 40° to 50°. The resulting gum was dissolved in 30 cc. of chloroform. Ten cc. of this solution was treated with 1 cc. of water and enough ethyl alcohol to make a homogeneous solution. Crystals of the phosphonic acid soon began to separate. After 4 hours the precipitate was filtered off; weight 1.7 g., or 61%.

The remaining 20 cc. of solution was treated with 2.9 g. of bromine which it decolorized without evolution of hydrogen bromide. The solution was then treated with 2 cc. of water and 30 cc. of alcohol. After 48 hours the solid was filtered off; 2.7 g. of mixed bromides, m. p. 160° to 170°, was obtained.

(b) Five g. of benzal-acetophenone, 4.5 g. of phosphenyl chloride and 3.5 g. of acetic anhydride were allowed to react as in (a), except that the mixture stood overnight. The solution was diluted to 25 cc. with acetic anhydride. Five cc. of this solution was poured into water; a white precipitate resulted. It was separated, dissolved in sodium hydroxide solution and reprecipitated with acid; 1.6 g. of phosphonic acid, m. p. 220° to 225°, was thus obtained. This was a yield of 94%.

The remaining 20 cc. of solution was treated with 3.9 g. of bromine which was readily taken up, producing only a faint red color at the very end of the addition. The solution was poured into 500 cc. of water; a crystalline precipitate formed which was filtered off; 7 g. of mixed bromides was thus obtained, a yield of 85%. This mixture was separated in the same way as described in the account of the preparation of the bromo acids from the phosphonic acid; 3.3 g. of the low-melting isomer was obtained which melted at 149°. A mixed-melting-point determination showed that it was identical with the low-melting isomer prepared by the bromination of the keto-phosphonic acid. Only about 0.5 g. of high-melting isomer was obtained in the pure condition after recrystallization. Its identity was also established by a mixed-melting-point determination.

### Summary.

1. Benzal-acetophenone reacts with phosphenyl chloride in glacial acetic acid producing a keto-phosphonic acid and acetyl chloride.

2. In acetic anhydride solution the product is an unsaturated cyclic anhydride which readily reacts with water forming the keto-phosphonic acid.

3. The structure of this anhydride follows from the fact that it combines with one equivalent of bromine and the product with water gives two stereo-isomeric  $\beta$ -bromoketo-phosphonic acids. These  $\beta$ -bromo acids were also prepared by bromination of the keto-phosphonic acid.

4. Both  $\beta$ -bromo acids decompose in the presence of aqueous alkali to give benzal-acetophenone, hydrogen bromide and phenylphosphonic acid. This proves they are stereo-isomeric and are  $\beta$ -bromo compounds.

5. The structure of the compound formed in acetic anhydride shows that the first step in the process is the 1,4 addition to the conjugated system of the phosphorus atom of the phosphenyl chloride.

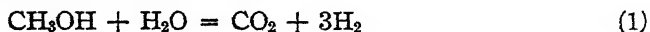
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COPENHAGEN.]

## A REACTION BETWEEN METHYL ALCOHOL AND WATER AND SOME RELATED REACTIONS.

By J. A. CHRISTIANSEN.

Received March 19, 1921.

In experiments on the synthesis of methyl alcohol I had observed that a mixture of steam and methyl alcohol vapor when passed through finely divided reduced copper reacts with the formation of hydrogen and carbon dioxide. To follow up this interesting reaction, I made some further experiments showing that the reaction



proceeds sensibly without side-reactions.

The reduced copper was made from copper oxide precipitated from a hot solution of copper sulfate by means of sodium hydroxide, and was contained in a vertical U-tube (of combustion glass about 20 cm. in height and 10 mm. in diameter, that could be heated in an oil-bath to about 300°. The upper end of one branch was bent in an angle of about 45°, while the upper end of the other was bent to a horizontal position.

From a buret a mixture of methyl alcohol and water was passed through the inclined tube. The velocity of the stream was regulated by a capillary through which it was forced by means of an air pressure of several centimeters of mercury. The horizontal tube was connected with a vertical cooling coil which served to condense the vapors of water, methyl alcohol, and other condensable compounds that passed over. The condensate was collected in a small suction flask with side-tube. From this the gases passed to two spiral absorption tubes containing sodium hydroxide to absorb the carbon dioxide. The non-absorbed gases were finally collected over water in a calibrated gas buret of 500 cc. capacity.

Between the suction flask and the absorption tubes a T-form stopcock was inserted, the free end of which dipped under water in a cylinder. By means of this device it was possible to sweep out the air of the suction flask, and to start and stop the collection of the gases at any given moment. Simultaneously the height of the liquid in the buret was noted, and so the quantity of alcohol solution, delivered during the period, was known.

In each experiment the quantities of carbon dioxide and formic acid (plus methyl formate) were determined by titration, the former according to Winckler's method. The mixture in the gas buret was analyzed by means of an Orsat apparatus.

As the air in the suction flask was displaced by the carbon dioxide-hydrogen mixture before the beginning of the experiment, the volume of hydrogen formed was found by subtracting the volume of diluted



alcohol used from the volume of gas collected, subject to a correction because the air was not totally displaced, and determined by the difference between the air found by analysis and the known volume of the air space in the absorption tubes. This was applied by subtracting  $\frac{1}{4}$  of the difference from the volume of hydrogen found. Of course all volumes were properly corrected for the influence of varying temperature, pressure and moisture content.

Only traces of free acid and carbon monoxide were found.

From these data the molecular proportion between the hydrogen and carbon dioxide formed during the reaction was calculated. In the first experiments this proportion was constantly found at about 2.8, but it appeared that the deviation was due to a piece of rubber tubing, several centimeters in length, inserted between the last absorption coil and the gas buret, through which the hydrogen diffused in spite of the fact that it was completely immersed in water. When this tubing was replaced by a glass tube, the proportion became exactly 3, indicating that the reaction proceeds practically without side reactions according to Equation 1.

The following is a typical experiment.

The alcohol (about 99%) was diluted 1 to 10 by volume. The temperature of the oil-bath was  $255^{\circ} \pm 1^{\circ}$ . During 108 minutes 20.00 cc. of the liquid passed the apparatus.

	Cc.
Volume of gas collected, reduced to standard conditions, dry,	283.6
Correction for distillate	17.7
Correction for air displaced by CO <sub>2</sub>	0.7

Volume of hydrogen found 265.2

CO <sub>2</sub> found	
In 20 cc. of distillate	4.0
In the second absorption tube	1.1
In the first absorption tube	82.5
In gas (?)	0.5

Volume of carbon dioxide 88.1

Volume of hydrogen / Volume of carbon dioxide 3.01

Later it was found that formaldehyde also is hydrolyzed according to the analogous reaction



at a temperature of about  $235^{\circ}$  and with finely divided copper as a catalyst, but the experiments were of a more qualitative nature.

It is very probable that some of the hydrogen is used up in reduction of formaldehyde to methyl alcohol, so that the proportion of hydrogen to carbon dioxide will be smaller than 2, a result also indicated by the above experiments.

In this connection it may be of interest to note that the well known reaction



catalyzed by copper, according to an experiment of mine also proceeds with formation of an excess of carbon dioxide, presumably on account of reduction of formic acid.<sup>1</sup>

### Summary.

Experiments are reported showing that the reactions  $\text{CH}_3\text{OH} + \text{H}_2\text{O} = \text{CO}_2 + 3\text{H}_2$  and  $\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$  proceed when suitable vapor mixtures are led through finely divided reduced copper at temperatures about 230° to 250°.

COPENHAGEN, DENMARK.

[CONTRIBUTION FROM THE ABBOTT LABORATORIES.]

## PREPARATION AND HYDROLYSIS OF BENZYL ESTERS.

By E. H. VOLWILER AND E. B. VLIET.

Received March 24, 1921.

In his classical researches on the therapeutic properties of combined opium alkaloids, and particularly of the alkaloids of the papaverine group, Macht<sup>1</sup> found that the antispasmodic effect of these compounds is due to the benzyl nucleus. This discovery was followed by his investigation of two simple organic esters of benzyl alcohol, namely, benzyl acetate and benzyl benzoate. It was found that the former is undesirable due to gastric disturbances which it induces, whereas benzyl benzoate is quite effective in relaxing unstripped muscle, and is better tolerated than benzyl acetate.

Up to the present time benzyl benzoate is the only benzyl ester which has come into extended use, although benzyl stearate and benzyl succinate have recently been introduced. The chief obstacle in studying new benzyl esters is the difficulty of determining the relative merits of the various esters by any methods that are rapid and fairly accurate. The general insolubility of the esters in water makes pharmacological tests difficult. Hence, in determining the comparative values of new benzyl esters, actual clinical use has always been necessary in spite of the length of time and of the uncertainties incident to such examinations.

A rapid chemical method of gaining a preliminary idea of the value of these esters would be extremely desirable. In devising such a test, it would be necessary to know whether the effect of benzyl esters is due to the entire benzyl ester molecule or to benzyl alcohol formed by hydrolysis of the ester in the body. The fact that benzyl benzoate and benzyl

<sup>1</sup> Cf. Sabatier, "Die Katalyse in der organischen Chemie," Leipzig, 1914, p. 151.

<sup>1</sup> Macht, *J. Pharmacol.*, 9, 287 (1917); 11, 389-446 (1918).

acetate are excreted as hippuric acid and that benzyl alcohol itself has a relaxing effect on unstripped muscle<sup>2</sup> seems to indicate that the effect is due, to some extent at least, to the hydrolysis of the esters. If it develops that the action is due to the benzyl alcohol split off in the body by hydrolysis, it is very probable that the therapeutic effects would be proportional to the rates of hydrolysis of the esters. On the other hand, if the effect is due to the intact benzyl ester molecule, the esters that are more slowly hydrolyzed in the body would probably have the more pronounced action.<sup>3</sup>

We have, therefore, determined the rates of hydrolysis of a number of benzyl esters in dil. alcoholic potassium hydroxide solution. A comparison of these data with the corresponding pharmacological and clinical tests should go far towards indicating the basis on which the therapeutic action of these compounds rests.

The benzyl esters investigated were the benzoate, acetate, cinnamate, salicylate, *p*-aminobenzoate, stearate, fumarate, succinate and acetyl-salicylate.

#### Preparation of the Esters.

Good grades of commercial benzyl benzoate (boiling at 222 to 225°, at 40 mm.) and benzyl acetate (boiling at 210 to 213°, at 745 mm.) were used. Benzyl stearate (melting at 40 to 42°) was furnished by Eli Lilly and Company and benzyl succinate (melting at 41 to 43.5°) by Frederick Stearns and Company.

Benzyl fumarate was prepared from fumaric acid and benzyl alcohol by the method of Bischoff and Hedenström<sup>4</sup> and purified by recrystallizing twice from alcohol. A product was obtained boiling at 210 to 211° at 5 mm. and melting at 58.5 to 59.5°.

Benzyl salicylate<sup>5</sup> was prepared by heating sodium salicylate with a slight excess of benzyl chloride and a small amount of diethylamine in an oil-bath at 130 to 140° for 17 hours. Upon cooling, the mixture was washed with water, the excess of benzyl chloride was removed by steam distillation and the remaining oil was distilled in a vacuum. Practically the entire amount came over between 165° and 192° at 7 mm. Upon redistilling, a yield of 85% of a product boiling at 170 to 175° at 7 mm. was obtained. In this reaction a temperature higher than 140° causes the formation of high-boiling side products while the absence of diethylamine as a catalyst greatly decreases the yield.

<sup>2</sup> Macht, *J. Pharmacol.*, **11**, 263 (1918).

<sup>3</sup> Pharmacological tests on these esters have been carried out in the Department of Pharmacology, of the Abbott Laboratories and published. Nielsen and Higgins, *J. Lab. Clin. Med.*, **6**, No. 7, April (1921); **6**, No. 12, Sept. (1921).

<sup>4</sup> Bischoff and Hedenström, *Ber.*, **35**, 4089 (1902).

<sup>5</sup> Aktien Gesellschaft, *Friedlaender.*, **6**, 1108; (Ger. pat. 119, 463); Gomberg and Buchler, *THIS JOURNAL*, **42**, 2065 (1920).

Benzyl cinnamate<sup>6</sup> was prepared in a manner similar to that for benzyl and after purification by repeated fractional distillation in a vacuum salicylate product was obtained which boiled at 228 to 230° at 22 mm. and crystallized as a white solid melting at 33 to 34°.

Benzyl acetylsalicylate was prepared by heating a mixture of 50 g. of benzyl salicylate, 30 g. of acetic anhydride and 10 g. of finely pulverized anhydrous sodium acetate on a boiling-water bath for 2 hours. The mixture was then cooled, taken up in benzene, washed with dil. sodium hydroxide solution and water; and after drying with calcium chloride the benzene was distilled, leaving a very viscous liquid. This was placed out of doors overnight at a temperature of about 20° whereupon it solidified. The material was purified by dissolving in hot ligroin from which, upon cooling, triturating and inoculating, 40 g. of a white solid was obtained melting at 25 to 25.5°. A portion of this was recrystallized several times from petroleum ether containing a little carbon tetrachloride and a product was obtained melting at 25.5 to 26°. The product is extremely soluble in benzene, xylene, carbon tetrachloride, acetone and ethyl acetate but is only slightly soluble in cold petroleum ether and ligroin. It boils at 197 to 200° at 7 mm.

Subs., 0.1347: CO<sub>2</sub>, 0.3505; H<sub>2</sub>O, 0.0644. Calc. for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>: C, 71.08; H, 5.22. Found: C, 70.96; H, 5.35.

Benzyl-*p*-aminobenzoate was prepared from benzyl *p*-nitrobenzoate. The nitro ester was prepared by heating 50 g. of sodium *p*-nitrobenzoate, 50 g. of benzyl chloride and 2 cc. of diethylamine in an oil-bath at 130° for 24 hours. Upon cooling, the mixture was taken up in water and benzene. The residue obtained from the benzene layer was freed from benzyl chloride by steam distillation and further purified by two crystallizations from 95% alcohol. An 85% yield of a product melting at 82 to 83° was thus obtained.

The nitro ester was reduced with iron and hydrochloric acid. After two crystallizations from carbon tetrachloride, the solid material had only a faintly yellow tinge and melted at 88.5° to 89.5°. From 42 g. of nitro ester, 25.5 g. of purified benzyl *p*-aminobenzoate was obtained.

Calc. for C<sub>14</sub>H<sub>13</sub>O<sub>2</sub>N: N, 6.17. Found (Kjeldahl): 5.89.

The hydrochloride was prepared by treating an ether solution of the purified base with alcoholic hydrochloric acid. This gave a beautiful white solid melting at 188 to 189° with the formation of some gas.

Shonle and Row<sup>7</sup> give the melting point of the hydrochloride as 1 and state "the free base is a yellow viscous liquid having no definite melting point and becoming wax-like on standing."

<sup>6</sup> Grimaux, *Z. Chem.*, 5, 157 (1869); Kalle and Co., *Friedlaender*, 6, 1234, Ger 127,649; Gomberg and Buchler, *loc. cit.*

<sup>7</sup> Shonle and Row, *THIS JOURNAL*, 43, 364 (1921).

### Hydrolysis.

The velocity of saponification of the esters was determined by a method similar to that used by Bischoff and Hedenström.<sup>8</sup> A definite amount of ester was dissolved in 20 cc. of acetone, and 50 cc. of 0.0633 *N* potassium hydroxide solution in 97% alcohol was added, the temperature being kept at 20°. At regular intervals 5-cc. portions were pipetted from the mixture and the excess of potassium hydroxide was titrated with 0.02 *N* hydrochloric acid, using phenolphthalein as indicator. The ratio of the number of moles of ester to the number of moles of potassium hydroxide varied according to the nature of the ester. With esters of dibasic acids, such as fumaric and succinic, two moles of potassium hydroxide were used to one mole of ester while the ratio with esters of mono-basic acids (benzoic, acetic, etc.) was 1:1.

Benzyl salicylate was treated in a slightly different manner, because of the acidic hydroxyl group which holds one mole of potassium hydroxide as long as an excess of alkali is present. Therefore, potassium hydroxide approximately twice as concentrated as that used in the other tests was employed for the salicylate and that for the benzyl acetylsalicylate was about three times as concentrated. A run was made with acetylsalicylic acid in order to determine the rate of hydrolysis of the acetyl group alone, so that the velocity of saponification of the benzyl group in benzyl acetylsalicylate could be estimated.

An attempt was made to determine the rate of saponification of benzyl *p*-aminobenzoate but this proved to be impossible by the method used because the amino group in the free acid is strongly basic, while the amino group in the ester is practically neutral. Hence, the same amount of hydrochloric acid was required to neutralize the mixture, regardless of the extent to which the hydrolysis had proceeded. That hydrolysis had actually occurred was evidenced by the fact that during the first few hours a precipitate was obtained when the alcohol-acetone reaction mixture was diluted with water, whereas after 24 hours, no precipitate formed under these conditions.

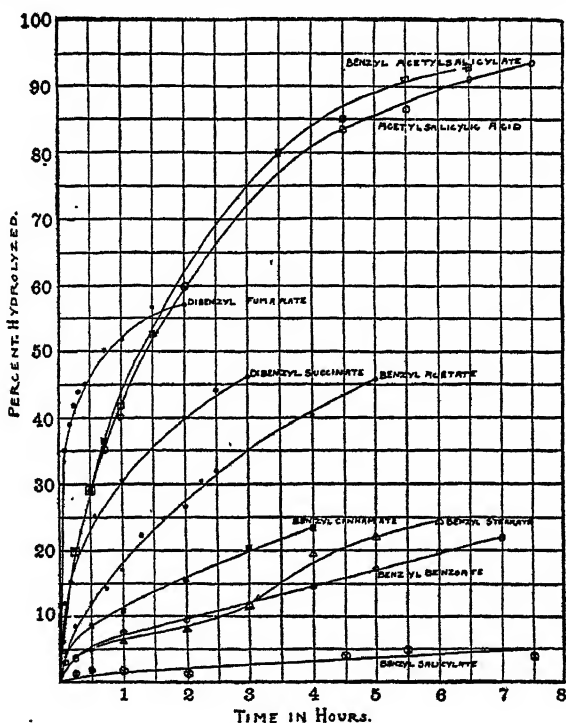
Duplicate runs were made in nearly all cases, which indicate that the results are accurate within about 3%. The results are shown by the accompanying curves.

The irregularity of the curve for benzyl stearate is perhaps due to the fact that a precipitate of potassium stearate separated from the reaction mixture after hydrolysis had proceeded for about 3 hours. This would tend to decrease the concentration of the reaction products and allow the hydrolysis to proceed more rapidly. A check run showed close agreement at all points. No precipitate formed from any of the other esters.

The result for benzyl acetylsalicylate is calculated so that if both the

<sup>8</sup> Bischoff and Hedenström, *Ber.*, 35, 3433 (1902).

acetyl and benzyl groups were completely hydrolyzed, the result would be 200%. The difference between these values and those for acetylsalicylic acid alone should give the velocity of hydrolysis of the benzyl group,



assuming that the rate of hydrolysis of the acetyl group is the same for both compounds. This seems to be true, for the difference is approximately equal to the rate of hydrolysis of the benzyl group in benzyl salicylate.

### Summary.

1. The comparative rates of hydrolysis of benzyl benzoate, acetate, cinnamate, salicylate, stearate, fumarate, succinate and acetylsalicylate were determined in order to obtain a basis for the correlation of chemical properties and physiological action.

2. The rates of hydrolysis of these benzyl esters increase in the following order: salicylate, benzoate, stearate, cinnamate, acetate, succinate and fumarate.

3. The results indicate that the rate of hydrolysis of the benzyl group in benzyl acetylsalicylate is of the same order as in benzyl salicylate.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

# ADDITION REACTIONS OF PHOSPHORUS HALIDES. III. THE REACTION WITH DIBENZAL-ACETONE AND CINNAMYLIDENE-ACETOPHENONE.

BY JAMES B. CONANT, ALBERT H. BUMP AND HAROLD S. HOLT.

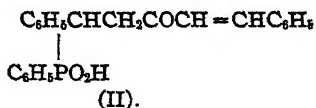
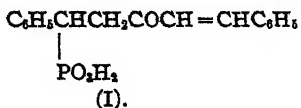
Received April 4, 1921.

Both phosphorus trichloride and phosphenyl chloride (phenyl-dichlorophosphine) readily combine with the conjugated system of simple unsaturated ketones such as benzal-acetophenone. The addition product reacts with glacial acetic acid and forms a saturated keto-phosphonic acid.<sup>1</sup> As a continuation of the study of these reagents on conjugated systems, two di-olefenic ketones—dibenzal-acetone and cinnamylidene acetophenone—have been investigated. Keto-phosphonic acids were obtained by the action of phosphorus trichloride on both substances but the yields were unsatisfactory. Phosphenyl chloride gave much better results; the yields were fairly good and the acids obtained were high melting, crystalline substances. This reagent, therefore, seems to be a promising one for the further investigation of unsaturated ketones.

Both reagents combine with only one of the two conjugated systems in dibenzal-acetone; it was not possible to obtain diphosphonic acids such as might be formed by the addition of a second molecule of the reagent. The addition to cinnamylidene-acetophenone takes place in the 1,4 position although there is the possibility of 1,6 addition with this compound. This is in agreement with the results obtained by adding other reagents to this same substance.

## The Reaction with Dibenzal-acetone.

The reaction between this ketone and the phosphorus halide was carried out in glacial acetic acid; no attempt was made to isolate any intermediate products, as the mechanism of the reaction has already been established. A dibasic keto-phosphonic acid (I) was obtained by the use of the trichloride and a monobasic acid (II) by the use of phosphenyl chloride.

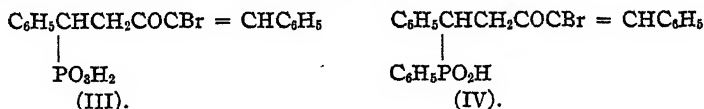


Both of these substances are unsaturated; they combine with two atoms of bromine and are readily oxidized with the formation of benzaldehyde. This establishes their structure. The monobasic acid (II) when oxidized with ozone yielded, besides benzaldehyde, a dibasic acid of the formula  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5\text{PO}_2\text{H})\text{CH}_2\text{COOH}$ . The first decomposition product of the

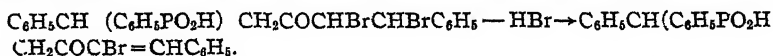
<sup>1</sup> THIS JOURNAL, 42, 830 (1920).

ozonide, an  $\alpha$ -ketonic aldehyde, could not be isolated, and under the conditions of the experiment, was apparently transformed into the saturated acid with one less carbon atom.

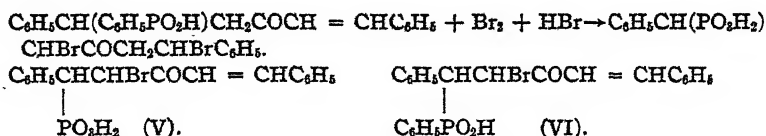
The dibromides which were formed from both acids (I) and (II), very readily lost hydrobromic acid when treated with alkaline reagents and formed unsaturated monobromo acids. The structure of these monobromides is as shown below (III and IV).



This structure is in accord with the well-known ease with which  $\beta$ -bromo ketones lose hydrobromic acid when treated with alkaline reagents.



The only other possibility is that the dibromide is not a real addition product but is formed by the substitution of one of the hydrogens of the  $\text{CH}_2$  group and subsequent addition of hydrobromic acid to the double bond. This hydrobromic acid would then be readily removed by alkaline reagents and the monobromides would have the structures represented by (V) and (VI).



In view of the somewhat unusual behavior of these monobromides with alkaline reagents, it was necessary to decide definitely between these alternative formulas. This was accomplished by oxidation with ozone. The dibasic monobromide (III or V) yields a tribasic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{PO}_3\text{H}_2)\text{CH}_2\text{COCO}_2\text{H}$ ; on heating, it is transformed into a substance the analysis of which is in agreement with the formula  $\text{C}_6\text{H}_5\text{CH}(\text{PO}_3\text{H}_2)\text{CH}_2\text{CO}_2\text{H}$ . Such acids could result only by the oxidation of a compound represented by Formula III; a substance with the alternative structure (V) would yield an  $\alpha$ -bromo acid. Furthermore, the first decomposition product of the ozonide of a substance of Structure III should be an acid bromide. This could not be isolated but its presence was shown by the fact that hydrobromic acid was formed when the ozonized solution was shaken with cold water.

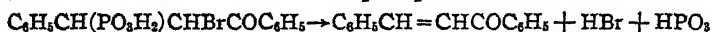
In the case of the other monobromo acid (IV or VI), hydrobromic acid was formed as before, but the ketonic acid could not be isolated. Its decomposition product  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5\text{PO}_2\text{H})\text{CH}_2\text{COOH}$ , however, was obtained and found to be identical with the acid formed by oxidation of the



keto-phosphonic acid (II). This establishes the structure of the monobromide as being that represented by Formula IV. The addition of bromine to the unsaturated acids thus proceeds normally.

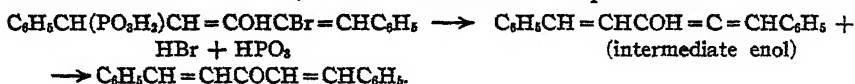
### Reactions of the Monobromides.

Certain  $\beta$ -bromophosphonic acids which have been previously described<sup>1</sup> are very unstable in the presence of aqueous alkaline reagents. For example, the bromo acid prepared from benzal-acetophenone is decomposed even by sodium hydrogen carbonate solution forming the unsaturated ketone, sodium bromide and sodium phosphate.



It was therefore of interest to investigate the action of alkaline reagents on the bromides prepared in this research. The dibromide dissolves in cold sodium hydrogen carbonate or carbonate solution without decomposition. On warming these solutions, however, decomposition takes place, the odor of benzaldehyde becoming at once apparent. Both dibromides can be transformed into monobromides as previously stated. This is accomplished by the use of one equivalent of potassium hydroxide, or better by an excess of potassium acetate.

The monobromo acids readily dissolve in sodium carbonate solution without decomposition. Aqueous potassium hydroxide solutions of the acids, however, decompose quite rapidly with the formation of benzaldehyde and the removal of bromine and the phosphorus radical. No other definite products could be isolated with the monobasic acid (IV). In the case of the dibasic acid (III), however, a small amount of dibenzalacetone was formed. The use of alcoholic potassium hydroxide solution increased the yield of unsaturated ketone to 25%. This formation of the unsaturated ketone is most surprising. No evidence for the mechanism of the reaction is at hand but in view of the results obtained with the  $\beta$ -bromo acids it seems probable that a simultaneous removal of the bromine atom and the phosphate group is involved. If this elimination took place from the enol form of the keto-acid, it would be a usual case of 1,4 elimination—the reverse of 1,4 addition. Subsequent ketonization of the product would form dibenzalacetone. Considering the fact that this decomposition takes place under conditions which would favor the formation of the enol form, this mechanism seems probable.

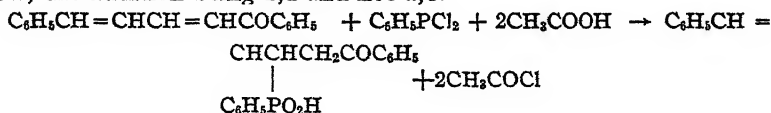


The formation of benzaldehyde as another product of this reaction can be attributed to the further decomposition of the unsaturated enol form. The easy decomposition of both these dibromides with the formation of benzaldehyde must be in some such way connected with the presence of the

bromine atom. The unsaturated keto-phosphonic acids themselves are not decomposed under parallel conditions.

### Reaction with Cinnamylidene-acetophenone.

The results obtained with the trichloride and this ketone were very unsatisfactory; a keto-phosphonic acid was obtained but in very small amounts. Phosphenyl chloride, however, gave fair yields. The structure of the product was shown by oxidation with ozone. Benzaldehyde was obtained in large quantities. The reaction thus takes place as shown below, the addition being 1,4 and not 1,6.



### Experimental.

$\alpha$ -Phenyl- $\beta$ -cinnamoyl-ethyl-phosphonic Acid,  $\text{C}_6\text{H}_5\text{CH}(\text{PO}_2\text{H}_2)\text{CHCOCH}=\text{CHC}_6\text{H}_5$ .—This substance was prepared as previously described<sup>2</sup> by the action of phosphorus trichloride on dibenzal-acetone in glacial acetic acid. In attempting to prepare considerable quantities of this acid it was found desirable to crystallize it from hot dil. acetic acid. Considerable amounts of some oily impurities were thus eliminated and the pure acid containing 1.25 mols. of water of crystallization was obtained. The yields were low; about 25% being the average. The rest of the material was apparently converted into some other acidic substance which could not be obtained in crystalline condition.

The acid is not decomposed by alcoholic potassium hydroxide solution either hot or cold. A crystalline potassium salt separates, from which the acid may be obtained by treatment with acid.

Attempts to add another molecule of phosphorus trichloride to this unsaturated ketonic acid failed. Both acetic acid and anhydride were employed as mediums but the monophosphonic acid was recovered unchanged after treatment of the reaction mixture with water. In one experiment the reaction mixture was heated to somewhat below 100°. On treatment with water no unchanged monophosphonic acid could be obtained; the entire product was soluble in water. This points to the formation of a diphosphonic acid, but no substance could be isolated from the water solution.

$\alpha$ -Phenyl- $\beta$ -cinnamoyl-ethyl-phenylphosphonic Acid,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5\text{PO}_2\text{H})\text{CHCOCH}=\text{CHC}_6\text{H}_5$ .—Five g. of dibenzal-acetone was suspended in 5 cc. of glacial acetic acid, and 3 cc. (one equivalent) of phosphenyl chloride was added to the mixture. On standing a few moments the ketone dissolved and the fumes of acetyl chloride were noticeable. Within 5 minutes the mixture solidified. The solid was then dissolved by treatment with an excess of 20% sodium hydroxide solution. The aqueous solution was extracted with ether to remove any unchanged ketone and the phosphonic acid precipitated by the addition of hydrochloric acid. The solid was filtered, washed with water and recrystallized from hot glacial acetic acid. The average yield was 53%. The pure substance melts at 235 to 236°; it is almost insoluble in all common solvents.

*Analysis.* Calc. for  $\text{C}_{23}\text{H}_{21}\text{O}_4\text{P}$ : P, 8.3. Found: 8.1.

*Oxidation with ozone.*—One g. of the acid was suspended in 50 cc. of chloroform, and a stream of ozonized oxygen bubbled through the mixture. The ozonized oxygen was

<sup>2</sup> THIS JOURNAL, 39, 2679 (1917).

prepared by electrolysis and was analyzed from time to time by passing a certain amount of it through potassium iodide solution. The gas contained about 4% of ozone, but was not completely free from moisture in spite of passing through a tube of phosphorus pentoxide. The oxidation was considered as complete when about a 20% excess of the theoretical amount of ozone had been passed into the solution. The solvent was evaporated under diminished pressure at a temperature of 40°. The residue was then distilled with steam; 0.2 g. of benzaldehyde was thus obtained and identified by converting into the phenylhydrazone. The residue in the flask consisted of a water solution and a small amount (0.18) g. of gummy material. The water solution on evaporation yielded 0.4 g. of a crystalline solid melting at 212°.

$\alpha$ -Phenyl- $\beta$ -carboxy-ethyl-phenylphosphonic Acid,  $C_6H_5CH(C_6H_5PO_2H)CH_2CO_2H$ .—This acid, obtained as just indicated, could be recrystallized from hot water; it melted at 212°. Titration with 0.2 *N* sodium hydroxide solution showed it to be a dibasic acid with a molecular weight of 289 (calculated 290).

*Analysis.* Calc. for  $C_{13}H_{13}O_4P$ : P, 10.7. Found: 10.8.

$\alpha$ -Phenyl- $\beta$  (dibromo-hydrocinnamoyl)-ethyl-phosphonic Acid,  $C_6H_5CH(PO_2H)CH_2COCHBrCHBrC_6H_5$ .—This substance was prepared by the action of bromine on a chloroform solution of the corresponding unsaturated phosphonic acid. The reaction is accelerated by sunlight; no hydrogen bromide is evolved. The product crystallizes from moist chloroform or aqueous alcohol in fine white needles melting with decomposition at 180 to 182°. They contain 2.5 mols. of water of crystallization. The anhydrous material could be obtained as an oil by working in absolutely dry chloroform or by heating a suspension of the hydrated material in chloroform together with anhydrous calcium chloride. Since the dibromide on heating loses hydrobromic acid as well as water, no direct determination of the water of crystallization was possible. The hydrated material is not soluble in chloroform but can be crystallized from aqueous alcohol.

*Analysis.* Calc. for  $C_{17}H_{17}PO_4Br_2 + 2.5H_2O$ : Br, 30.7. Found: 30.7, 30.6, 30.8.

$\alpha$ -Phenyl- $\beta$ -( $\alpha$ -bromo-cinnamoyl)-ethyl-phosphonic Acid,  $C_6H_5CH(PO_2H)CH_2COCBr=CHC_6H_5$ .—7 g. of the crude crystalline dibromide was suspended in 150 cc. of 95% alcohol and treated with a solution of 3 g. of potassium hydroxide in 100 cc. of 95% alcohol. The mixture was allowed to stand for 2 hours; a considerable amount of potassium bromide separated. The solution was then diluted with an equal volume of water. The small precipitate of dibenzal-acetone (0.1 g.) which formed was filtered off. (This substance was produced by the action of the excess of potassium hydroxide on the monobromide as described later.) The filtrate was acidified and the monobromide precipitated in the form of fine needle crystals. They were recrystallized from aqueous alcohol containing a little acetic acid. 4.5 g. was thus obtained, a yield of 81%. The material thus prepared contains water of crystallization; it melts with the loss of this water at 130 to 132°. It is readily soluble in sodium hydrogen carbonate solution without decomposition. It reduces alkaline potassium permanganate solution instantly but does not combine with bromine. Titration with 0.5 *N* sodium hydroxide solution showed it to be a dibasic acid.

*Analysis.* Calc. for  $C_{17}H_{16}O_4BrP + 1H_2O$ : Br, 19.4. Found: 19.5, 19.4.

A sample of the acid was heated to constant weight at 135° and the resulting melt analyzed for bromine.

*Analysis.* Calc. for  $C_{17}H_{16}O_4BrP$ : Br, 20.2. Found: 20.3.

A sample of the dehydrated material was dissolved in dry ether and saturated with hydrogen bromide. On evaporation an oil was left, which, on treatment with 50% aqueous alcohol yielded the crystalline dibromide previously described. It was identified by a mixed-melting-point determination.

*Oxidation with Ozone.*—One g. of the monobromide was heated to constant weight at 120° and then dissolved in dry chloroform. The solution was treated with ozonized

oxygen in the manner previously described. The solution became red during the process due to the formation of free bromine. This was apparently formed by the hydrolysis of the acid bromide and oxidation of the hydrogen bromide by the ozone. At the end of the oxidation the solution contained a solid which was filtered off; it weighed 0.35 g. (50% yield). The chloroform solution was divided into two parts. One part was shaken with water and the aqueous layer tested for hydrobromic acid which was found to be present in large amount. The other half was evaporated and the residue distilled with steam; no benzaldehyde could be detected, but 0.1 g. of benzoic acid was obtained by crystallization from hot water. The free bromine apparently oxidized the aldehyde to the acid.

$\alpha$ -Phenyl- $\beta$ -glyoxy-ethyl-phosphonic Acid,  $C_6H_5CHPO_3H_2CH_2COCO_2H + 2H_2O$ .—The solid which separated from the ozonized solution melted at  $183^\circ$  with decomposition. Titration with 0.2 *N* sodium hydroxide solution showed that it was a tribasic acid with a molecular weight of 297; the calculated molecular weight is 294.

*Analysis.* Calc. for  $C_{10}H_{11}O_6P \cdot 2H_2O$ : P, 10.5. Found: 10.4.

A sample of the acid was heated to constant weight at  $120$ – $125^\circ$  and then analyzed.

*Analysis.* Calc. for  $C_9H_{11}O_6P$ : P, 13.5. Found: 13.2.

This shows that the ketonic acid on heating loses carbon monoxide and water and yields the acid  $C_6H_5CH(PO_3H_2)CH_2CO_2H$ .

$\alpha$ -Phenyl- $\beta$ -(dibromo-hydrocinnamoyl)-ethyl-phenylphosphonic Acid.—Five g. of the unsaturated monobasic phosphonic acid was suspended in chloroform and treated with bromine. The color of the bromine disappeared rapidly and no hydrobromic acid was evolved; after standing several hours the crystalline dibromide separated. The yield was almost quantitative. On recrystallization from hot glacial acetic acid, however, some material was lost; m. p.  $195^\circ$  with decomposition. The acid dissolves slowly in cold sodium hydrogen carbonate or carbonate solution and may be precipitated unchanged.

*Analysis.* Calc. for  $C_{22}H_{21}O_3Br_2P$ : Br, 29.8. Found: 29.6.

$\alpha$ -Phenyl- $\beta$ -( $\alpha$ -bromo-cinnamoyl)-ethyl-phenylphosphonic Acid.—The dibromide was dissolved in a hot 4% solution of potassium acetate in methyl alcohol. The solution was heated on the steam-bath for a few minutes and then poured into water. A clear solution resulted which on acidification yielded a crystalline precipitate of the monobromide. The yield was 80%; m. p.  $200^\circ$ .

*Analysis.* Calc. for  $C_{22}H_{20}O_3PBr$ : Br, 17.6. Found: 17.6.

*Oxidation with Ozone.*—The monobromide is almost insoluble in chloroform so that a suspension had to be used for the oxidation. Ozonized oxygen was passed through the mixture for many hours in order to complete the oxidation. 0.3 g. of material was oxidized in this way and the chloroform solution then extracted twice with water. The amount of hydrogen bromide in the aqueous layer was determined by the Volhard method.

*Analysis.* Calc. amount of bromide ion: 0.051 g. Found: 0.044 g. or 86%.

In another experiment 0.6 g. was ozonized and the chloroform solution extracted several times with water. The aqueous solution on evaporation to small volume yielded 0.17 g. of the dibasic acid melting at  $212^\circ$ , which was previously obtained by the oxidation of the unsaturated phosphonic acid. The identity of the material was established by mixed-melting-point determinations and titration with standard alkali.

A small amount of benzoic acid was obtained by evaporation of the original chloroform solution.

### The Action of Alkaline Reagents on the Monobromides.

Sodium hydrogen carbonate and sodium carbonate solutions dissolve

both monobromides without decomposition. On acidification the original material is recovered unchanged.

Aqueous 10% potassium hydroxide dissolves both monobromides but the solution soon becomes colored and the odor of benzaldehyde can be detected after the mixture has stood some minutes; small amounts of unsaturated ketone sometimes separate from the solution of the dibasic monobromo acid. No product except benzaldehyde could be identified with the monobasic monobromo acid. On acidification with nitric acid and addition of silver nitrate a heavy precipitate of silver bromide is obtained in every case.

Alcoholic potassium hydroxide rapidly decomposes both monobromides. The solutions become yellow and finally deep red; the odor of benzaldehyde is very evident. On dilution with water dibenzal-acetone is obtained in the case of the dibasic acid; no definite product could be isolated in similar experiments with the monobasic acid. A typical experiment with the dibasic monobromo acid as follows.

0.5 g. of monobromide was added to 20 cc. of 95 % alcohol containing 0.33 g. of dissolved potassium hydroxide. The solution turned yellow, and finally at the end of one hour, deep red. Potassium bromide was precipitated. The odor of benzaldehyde was noticed. After standing overnight the solution was diluted with three times its volume of water. A very fine crystalline precipitate of dibenzal-acetone separated and was filtered off and dried; 0.08 g. was thus obtained which is equivalent to 0.14 g. of the monobromide or 28% of the material used. It was identified by a mixed-melting-point determination.

$\alpha$ -Styryl- $\beta$ -benzoyl-ethyl-phosphonic Acid,  $C_6H_5CH = CHCH(PO_3H_2)CH_2COC_6H_5$ .—No satisfactory results could be obtained by using acetic acid as a medium for adding phosphorus trichloride to cinnamylidene-acetophenone. Acetic anhydride was therefore employed. 15 g. of the ketone was dissolved by gently warming in 15 g. of acetic anhydride. 18 g. of phosphorus trichloride was added to the warm solution and the flask gently warmed several times to the temperature at which acetyl chloride started to boil from the solution. The product after standing for 3 hours at room temperature was poured into 1800 cc. of water. The major portion of the product (about 10 g.) separated as an oil which could not be obtained in crystalline condition. It was completely soluble in sodium carbonate solution and was reprecipitated by acids. It was evidently a mixture of phosphonic acids but no definite substances could be isolated from it. The aqueous solution was decanted from the oil and evaporated to a small volume. About 1 g. of crystalline material was obtained which melted at 159 to 161°. It was soluble in sodium hydrogen carbonate and was oxidized by potassium permanganate solution with the formation of benzaldehyde. It decolorized a chloroform solution of bromine only slowly.

*Analyses.* Calc. for  $C_{17}H_{17}O_4P$ :  $1/4 H_2O$ : C, 63.6; H, 5.5; P, 9.8. Found: C, 63.7; H, 5.7; P, 9.7.

$\alpha$ -Styryl- $\beta$ -benzoyl-ethyl-phenylphosphonic Acid,  $= C_6H_5CH = CHCH(C_6H_5PO_3H)CH_2COC_6H_5$ .—Twenty g. of cinnamylidene-acetophenone was suspended in 20 cc. of glacial acetic acid, and 12 cc. of phosphenyl chloride was added. The ketone slowly dissolved. At the end of 3 hours the mixture was almost solid. The material was treated with water, the solid filtered and recrystallized from hot glacial acetic acid.

20.5 g. of recrystallized product was obtained,—a yield of 64%. The solid melts at 200°. It is insoluble in most solvents.

*Analysis.* Calc. for  $C_{23}H_{21}O_3P$ : P, 8.24. Found: 8.26.

*Oxidation with ozone.*—One g. of the material was suspended in chloroform and treated with ozonized oxygen for the calculated length of time. The solvent was evaporated and the residue distilled with steam. 0.22 g. of benzaldehyde was thus obtained, and 0.1 g. of unoxidized material was found in the residue. The amount of benzaldehyde found is thus about 90% of the amount that could theoretically be obtained from the 0.9 g. of material which was oxidized. In another experiment the residue left after evaporation of the solvent was treated with sodium carbonate solution and filtered from a small amount of oil. On acidification with nitric acid a dark flocculent precipitate was formed. It could not be obtained pure enough for analysis, but it was obviously an acid and contained phosphorus.

### Summary.

1. Phosphorus trichloride and phosphenyl chloride combine with dibenzal-acetone in glacial acetic acid to form unsaturated keto-phosphonic acids.

2. The unsaturated acids thus formed combine with two atoms of bromine and form dibromides. The dibromides on treatment with alkaline reagents easily lose hydrogen bromide and form monobromo acids. The structure of these monobromides was established by oxidation with ozone.

3. The monobromides are easily decomposed by aqueous and alcoholic potassium hydroxide. Benzaldehyde is formed. In the case of one of the monobromides about 25% of dibenzal-acetone is also produced.

4. Unsaturated keto-phosphonic acids are formed by the action of phosphorus trichloride and phosphenyl chloride on cinnamylidene-acetophenone in suitable solvents. The combination takes place in the 1,4 position as shown by oxidation with ozone.

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## THE ACTION OF HYDROGEN PHOSPHIDE ON FORMALDEHYDE.

BY ALFRED HOFFMAN.

Received April 18, 1921.

The condensation of hydrogen phosphide with aldehydes was studied by Messinger and Engels.<sup>1</sup> By passing a mixture of hydrogen phosphide and dry hydrogen chloride into ethereal solutions of the aldehydes they obtained compounds of the composition  $(R.CHO)_4PH_4Cl$ . Treated with potassium hydroxide these gave products assumed by the authors to be mixtures of the free phosphine and its hydrate. Similar compounds have been prepared by Girard,<sup>2</sup> by the action of phosphonium iodide on aldehydes. Formaldehyde was not investigated by either of these authors.

<sup>1</sup> Messinger and Engels, *Ber.*, 21, 325 (1888).

<sup>2</sup> Girard, *Ann. chim.*, [6] 2, 2 (1884).

In the experiments here described, it was found that hydrogen phosphide is readily absorbed when passed into a warm, aqueous solution of formaldehyde acidified with hydrochloric acid. On evaporation the solution gives a crystalline salt, which has the properties of a tetrahydroxymethylene-phosphonium chloride,  $(\text{HOCH}_2)_4\text{PCl}$ .

This substance is quite stable; its aqueous solution may be boiled without decomposition and it is unaffected by dil. acids. It reduces silver nitrate solution in the cold and is easily oxidized by conc. nitric acid. It is extremely sensitive toward alkalis and even neutral carbonates. With caustic soda solution, even in the cold, a vigorous evolution of hydrogen takes place. When the latter is completed by heating, it is found that exactly four atoms of hydrogen are split off. When this experiment was performed in an open tube, a slight odor of methyl alcohol was detected. If the solution is then acidified with hydrochloric acid and distilled to dryness, half a molecule of formic acid comes over. The residue of the molecule containing the phosphorus is more easily isolated when the decomposition is carried out with barium hydroxide. After removing the barium and evaporating, a thick colorless sirup remains which does not crystallize. According to the yield and to the percentage of phosphorus, the compound seems to have the empirical formula  $\text{C}_6\text{H}_9\text{O}_5\text{P}$ , perhaps constituted  $(\text{HOCH}_2)_3\text{PO}_2$ . As the course of the reaction and the constitution of the compound need further clearing up, the formula is given with due reserve. The reaction may be as follows,



The formaldehyde then reacts with the sodium hydroxide to give half methyl alcohol and half formic acid. The syrupy compound is rather difficult to oxidize with nitric acid. It has feeble acid properties, forming salts, with barium carbonate, for instance, which hydrolyze on evaporating the solution. By means of the Schotten-Baumann reaction the substance gives a well crystallizing tribenzoyl derivative.

With neutral carbonates, such as calcium carbonate the action is similar, but less vigorous, and there are indications of the formation of intermediate products. On adding the carbonate to the aqueous solution of the crystalline phosphonium chloride, an evolution of carbon dioxide is observed, due to the union of the chlorine with the calcium; then on heating, a slow evolution of hydrogen takes place and one molecule of formaldehyde distills. Also a disagreeable odor is noticed, perhaps the trihydroxymethylene-phosphine. It was not found possible to isolate these intermediate compounds either as such or as benzoyl derivatives. The final product in this case also was the syrupy compound.

Of special interest is the action of ammonia on the crystalline phosphonium chloride. If dil. aqueous solutions are employed, the ammonia acts like an alkali, hydrogen is evolved and the solution remains clear.

If, however, concentrated solutions are used, a curdy white precipitate is formed in small amount. By working under anhydrous conditions in methyl alcohol, larger yields are obtained; but the best yields, up to almost 50% of the weight of phosphonium chloride taken, are obtained in aqueous solution with ammonium chloride and a neutral carbonate or bicarbonate. As the substance contains almost twice as much phosphorus as the phosphonium chloride, the reaction is nearly quantitative. The ammonia derivative is a curdy, somewhat stringy, white precipitate. It is very voluminous and retains the bubbles of carbon dioxide from the carbonates, so that in fairly concentrated solutions a spongy, dough-like mass is obtained. The compound is insoluble in water, dilute acids and alkalis and all the ordinary organic solvents, but on boiling with water for several days it goes into solution, giving the ammonia salt of a complex organic phosphoric acid. It is easily soluble in cold dil. formaldehyde solution, giving a clear solution, which on evaporation leaves a spongy horn-like mass, having a pronounced fishy odor, like trimethylamine. The ammonia derivative is quite stable to heat. At a temperature far above 200°, it suddenly swells, gives off an odor of decayed fish and burns with a flame. With concentrated nitric acid it reacts violently, often catching fire. Its composition seems to vary somewhat. The percentage composition is phosphorus, 27 to 30%; nitrogen, 14.5 to 16.2%. The filtrate from the preparation of the ammonia derivative contains hexamethylene-tetramine, which could be isolated by extracting the dried residue from the solution with chloroform. Its amount corresponds roughly to one molecule of formaldehyde for each molecule of the phosphonium chloride taken, but seems to vary somewhat. The ammonia derivative is not formed from the syrupy compound. Considerable further study will be necessary to determine the constitution of the substance, as, to judge from its physical properties, it must be of high molecular weight. It may be mentioned that aniline gives a similar precipitate with the phosphonium chloride but urea does not. The work is being continued.

### Experimental.

**Hydrogen Phosphide.**—To prepare this gas, small quantities of a mixture of two parts aluminum powder and one part red phosphorus were prepared on a piece of paper on an asbestos pad. On igniting the paper, the mixture became white-hot and there resulted a spongy mass of aluminum phosphide.<sup>3</sup> This substance reacts with cold water to give a steady stream of hydrogen phosphide. The gas so formed is not spontaneously inflammable at room temperature, but does ignite at the temperature of the following experiment (80°), causing small explosions in the apparatus.

**Tetrahydroxy-methylene-phosphonium chloride.**—A mixture of 90 cc. of 40 % formaldehyde solution and 40 cc. of hydrochloric acid, (sp. gr. 1.2) was introduced into a 100-cc. 3-bulb Ladenburg flask (it should fill about half of the neck of the flask), the latter provided

<sup>3</sup> Fonze-Diacon, *Compt. rend.*, 130, 1314 (1900); Bodroux, *Bull. soc. chim.*, [3] 27, 568 (1902).



with a stopper through which passed a gas-delivery tube reaching to the bottom. The flask was then inclined to an almost horizontal position, hydrogen phosphide was passed in to displace the air and the solution then heated to about  $80^{\circ}$ . At lower temperatures the reaction is correspondingly slower and at higher temperatures the vapor pressure of the solution interferes with the absorption. The bulbs of the flask serve to hold back the gas and make the reaction more complete. Hydrogen and some hydrogen phosphide escape from the side-neck and should be led off to a flue. Using 10 portions of each 4 g. of aluminum and 2 g. of phosphorus, the reaction was complete in two days. The liquid was evaporated on the steam-bath, with stirring toward the end until a white granular mass was obtained; yield, 50 g. (calculated yield, 57 g.). This is pure enough for preparative purposes. For analysis it was crystallized from glacial acetic acid, 1 g. of substance to 50 g. of acid. It crystallizes in flat needles of low melting point containing acetic acid of crystallization, which can be removed in a current of dry air at  $100^{\circ}$ . The pure substance melts at  $151^{\circ}$ , is very deliquescent, easily soluble in methyl alcohol, slightly in hot chloroform and insoluble in ether. It reacts with acetyl chloride and acetic anhydride to give oily products.

*Analysis.* Subs., 0.198: AgCl, 0.150. Subs., 0.217:  $Mg_2P_2O_7$ , 0.127. Calc. for  $C_4H_{12}O_4P_2Cl$ : Cl, 18.6; P, 16.2. Found: Cl, 18.68; P, 16.1.

**Action of Sodium Hydroxide.**—*Analysis.* Subs., 0.175: 44.7 cc. moist hydrogen at  $12^{\circ}$ , 750 mm. = 41.6 cc. dry hydrogen at  $0^{\circ}$ , 760 mm. Calc. for two molecules of hydrogen: 41.1 cc.

After acidifying with hydrochloric acid and distilling to dryness, the distillate was neutralized and treated with mercuric chloride solution.<sup>4</sup>

*Analysis.* Subs., 0.976:  $Hg_2Cl_2$ , 1.315 = 0.128 g. formic acid. Calc. for 0.5 molecule formic acid: 0.118 g.

**Action of Barium Hydroxide.**—*Analysis.* Subs., 0.691, treated with barium hydroxide solution and the barium removed quantitatively, gave 0.556 g. of syrup dried to constant weight. Calc. for  $C_3H_5O_3P$ : 0.567 g. 0.526 g. of sirup gave 0.364 g.  $Mg_2P_2O_7$ . Calc. for  $C_3H_5O_3P$ : P, 19.8. Found: 19.3.

**Action of Calcium Carbonate.**—*Analysis.* Subs. 1.008 in aqueous solution distilled with calcium carbonate and the distillate treated with a solution of mercuric chloride, sodium hydroxide and sodium sulfite<sup>5</sup> gave 1.116 g. Hg. Calc. for one molecule formaldehyde: 0.159. Found: 0.167.

**Preparation of the Tribenzoyl Derivative of the Syrupy Compound.**—The crystalline phosphonium chloride was boiled with a large excess of sodium hydroxide solution, (1–10), until no more hydrogen was given off, and the solution was cooled and shaken with a slight excess of benzoyl chloride until the oil solidified. Fine needles were obtained on crystallization from methyl alcohol, m. p.  $111^{\circ}$ , easily soluble in hot methyl alcohol but insoluble in water.

*Analysis.* Subs., 0.402 g:  $Mg_2P_2O_7$ , 0.100. Calc. for  $(C_6H_5COOCH_2)_3PO_2$ : P, 6.62. Found: 6.94.

### Summary.

The action of hydrogen phosphide on a warm, aqueous solution of formaldehyde, acidified with hydrochloric acid, was studied and the reaction product tetrahydroxy-methylene-phosphonium chloride isolated and its properties studied. By the action of alkalis or carbonates on the

<sup>4</sup> "Beilstein," 4th ed. Vol. II, p. 13.

<sup>5</sup> "Beilstein," 4th ed. Vol. I, p. 570.

latter, a compound,  $C_3H_5O_3P$ , was formed and its tribenzoyl derivative prepared. The action of ammonium chloride and calcium carbonate on tetrahydroxy-methylene-phosphonium chloride was studied and an insoluble curdy precipitate containing about 30% of phosphorus and 15% of nitrogen obtained.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, UNIVERSITY OF MINNESOTA.]

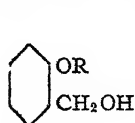
### SOME DERIVATIVES OF SALIGENIN.<sup>1</sup>

By MERRILL C. HART AND ARTHUR D. HIRSCHFELDER.

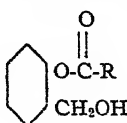
Received April 20, 1921.

Since Hirschfelder, Lundholm and Norrgaard<sup>2</sup> have shown that saligenin (*o*-hydroxy-benzyl alcohol) possesses valuable properties as a local anesthetic it was thought that an investigation of some of the derivatives of saligenin might also prove valuable. In this study it is desired to vary the saligenin molecule in several different ways and to study pharmacologically the different properties of the derivatives.

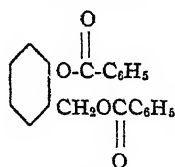
The saligenin molecule was first altered by varying the phenolic hydroxyl and simple ethers (Formula I) were synthesized. In this case ethers where R was both aliphatic and aromatic were prepared. The ethyl



(I).



(II).



(III).

propyl, *n*-butyl, *iso*-amyl, and the benzyl ethers of saligenin were made.

Other variations of the molecule were then prepared by making the esters of saligenin (Formula II) upon the phenolic hydroxyl. Representatives of this class of compounds were made by preparing the mono-acetate and the monobenzoate of saligenin. The mono-acetate was particularly desired because of its relation to acetyl salicylic acid (aspirin).

Also a derivative of saligenin, the dibenzoate, was prepared as a representative of the case where both the groups in the saligenin molecule were masked (Formula III).

The saligenin molecule was next modified by varying the nucleus. As the simplest and easiest way of doing this seemed through the introduction

<sup>1</sup> This work was done with the aid of funds granted by the United States Interdepartmental Board, for the investigation of the antiseptic and chemotherapeutic action of phenolic alcohols and their derivatives upon the gonococcus and the spirochaete.

<sup>2</sup> Hirschfelder, Lundholm and Norrgaard, *Science, N. S.*, 51, 21 (1920); *J. Pharmacol.* 15, 263 (1920).

of halogen into the nucleus, the monobromo and mono-iodo saligenin were prepared. It was necessary to produce these in fairly large quantities because they were used not only for pharmacological and clinical study, but they were found also to react slowly with mercuric acetate in dilute alcohol solution with the formation of mercury derivatives. It was desired to study these mercury derivatives both chemically and pharmacologically in comparison with the mercury derivative of saligenin.<sup>3</sup>

Of the ethers of saligenin (Formula I) we found that Cannizaro and Koerner<sup>4</sup> had prepared the methyl ether by treating molecular quantities of saligenin and potash in methyl alcohol with methyl iodide. Later this work was repeated by Pschorr, Wolfes and Buckow.<sup>5</sup> The methyl ether is an oil boiling at 240° with a pleasant ethereal odor.

Bötsch<sup>6</sup> prepared the ethyl ether of saligenin by heating an aqueous solution of saligenin with the theoretical amount of potassium hydroxide and ethyl iodide in a sealed vessel for 3 hours at 100°.

In this research the saligenin ethers were prepared by refluxing potassium saligenate with alkyl or aryl halides. The monosaligenin esters were made by the action of acid chlorides or acid anhydrides on potassium saligenate in ether or alcohol solutions. The dibenzoyl derivative may be prepared by the benzylation of saligenin in pyridine solution in the presence of calcium carbonate.

The methods of preparing monobromo-saligenin were studied and that of Auwers and Büttner<sup>7</sup> was found to be the best. The mono-iodo-saligenin has been made by Seidel<sup>8</sup> by treating saligenin in alcohol with iodine in the presence of mercuric oxide. We found that a better method for the preparation of this compound was to treat saligenin in water solution with a potassium iodide solution of iodine.

Most of the above syntheses required the use of potassium saligenate. This had been made by R. Rivals<sup>9</sup> but his method was not suitable for the preparation of potassium saligenate in quantity. We found that by treating saligenin in acetone solution with alcoholic potash, we could obtain practically theoretical yields of potassium saligenate.

### Experimental Part.

**Preparation of Potassium Saligenate.**—The saligenin used in these experiments was prepared according to the method given by us in a previous paper.

10 g. of pure saligenin was dissolved in 150 mls of acetone. To this was added 35 mls of a 25% solution of potassium hydroxide. A voluminous white precipitate

<sup>3</sup> Hart and Hirschfelder, *THIS JOURNAL*, 42, 2678 (1920).

<sup>4</sup> Cannizaro and Koerner, *Gazz. chim. ital.*, 2, 65-68 (1872).

<sup>5</sup> Pschorr, Wolfes and Buckow, *Ber.*, 33, 165 (1900).

<sup>6</sup> Bötsch, *Monatsh.* 1, 621 (1880).

<sup>7</sup> Auwers and Büttner, *Ann.*, 301-302, 131 (1898).

<sup>8</sup> Seidel, *J. prakt. Chem.*, 59, 105 (1899).

<sup>9</sup> R. Rivals, *Ann. chim., phys.*, 12, 556 (1897).

dried ether was then evaporated by a current of air. A white crystalline solid was obtained. The crystals were fine needles. This material was dried on a clay plate after having been extracted with a little petroleum ether. 18 g. (67.2% yield) was obtained. The melting point was 51°.

This substance was crystallized from 70% alcohol by taking it up in the alcohol at 50° and then cooling in a vacuum desiccator. When crystallized in this manner the dibenzoate came down as white feathery clusters of needle-like crystals. The melting point, 51°, was not raised by further crystallization.

This compound was very soluble in the usual organic solvents, very sparingly soluble in petroleum ether, and insoluble in water and glycerine. It gave no coloration with ferric chloride. On hydrolysis with alcoholic potash it gave benzoic acid, melting at 122°.

**Analysis of the Dibenzoate of Saligenin.**—The material from the crystallization from the dilute alcohol was dried to constant weight in a vacuum. A small sample was dissolved in 20 mls of 3% alcoholic potash and heated under a reflux condenser for 2 hours. Ten mls of water was added during the process of heating. At the end of this time the solution was diluted with 100 mls of water and extracted with ether. The alkaline solution was then made acid and extracted with ether thrice. The ether extracts were evaporated by a current of air and the residue dissolved in neutral alcohol and titrated with 0.1 *N* sodium hydroxide solution.

**Analysis.** Subs., 0.5153; 0.1 *N* NaOH, 30.84 mls. Calc. for  $C_6H_4(OCOC_6H_5)_2$  ( $CH_2OCOC_6H_5$ ):  $C_6H_5COOH$ , 73.49. Found: 73.07.

**Monobromo-saligenin** (2-hydroxy-5-bromo-benzyl alcohol).—This was prepared by the method of Auwers and Büttner.<sup>7</sup> Several other methods were tried for the preparation of this compound but the above gave the best results.

**Potassium Salt of Monobromo-saligenin.**—One g. of monobromo-saligenin was dissolved in 15 mls of acetone, and 2 mls of 25% alcoholic potash was added. A heavy white precipitate of the potassium salt of the monobromo-saligenin was obtained. It crystallized in fine white microscopic plates. It is extremely soluble in water, is soluble in alcohol, and is sparingly soluble in ether, petroleum ether, and acetone. On acidifying an aqueous solution of it crystalline microscopic plates of the monobromo-saligenin melting at 110° are obtained.

This potassium salt of monobromo-saligenin is also formed when monobromo-saligenin acetate (2-hydroxy-5-bromo-benzyl acetate) is treated in acetone solution with alcoholic potash.

**Mono-iodo-saligenin** (2-hydroxy-5-iodo-benzyl alcohol).—As Seidel<sup>8</sup> from 8.5 g. of saligenin obtained only 1 g. of the mono-iodo compound, it was quite necessary to find a method that would give greater yields. We found that a better method for the preparation of this compound was to treat saligenin in aqueous solution with a solution of iodine in 40% potassium iodide solution. 10 g. of saligenin was dissolved in 500 mls of water and to this was added a solution of 20 g. of iodine in 100 mls of 40% potassium iodide solution. This was allowed to stand for a week as much as possible in the sunlight. At the end of this time the solution was treated with solid sodium hydrogen carbonate until it turned light yellow. A pinkish white precipitate slowly formed and was filtered off. This precipitate was crystallized from hot water. Several extractions were necessary, the later yielding the purer product. The various crops obtained by this method melted from 128 to 130° in the case of the first, to 134 to 136° in the case of the last. Another crystallization from water was sufficient to give pure mono-iodo-saligenin melting at 138°. From 40 g. of saligenin, 12 g. of the pure mono-iodo-saligenin was obtained. This was in the form of white silky needles, melting at 138°.

**Potassium Salt of Iodo-saligenin.**—This was formed in a similar manner to that of the potassium salt of monobromo-saligenin. It consisted of fine white crystalline plates,

very soluble in water, soluble in alcohol, and sparingly soluble in acetone and petroleum ether. On treating an aqueous solution of it with acetic acid, crystals of the mono-iodo-saligenin, melting at 138° are obtained.

### Summary.

1. A method has been developed of treating saligenin in acetone solution with alcoholic potash by which practically theoretical yields of the potassium saligenate were obtained. This method was also used successfully in the preparation of the potassium salts of monobromo- and mono-iodo-saligenin.

By the reaction of potassium saligenate on ethyl iodide, the ethyl ether of saligenin identical with ethyl ether of saligenin prepared by Bötsch was prepared. In an analogous manner the propyl, *n*-butyl, *iso*-amyl, and benzyl ethers of saligenin were made.

3. The mono-acetate and the monobenzoate of saligenin were prepared from potassium saligenate and acetic anhydride and benzoyl chloride, respectively. The dibenzoate of saligenin was made by the benzoylation of saligenin in pyridine in the presence of calcium carbonate and with a slight excess of the benzoyl chloride.

4. The method of Auwers and Büttner for preparation of monobromo-saligenin by the bromination of saligenin in aqueous solution was found to give the best results.

5. For the preparation of mono-iodo-saligenin the best method found was the treatment of saligenin dissolved in water with an aqueous potassium iodide solution of iodine.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 359.]

## SOME ERRORS IN THE STUDY OF INVERTASE ACTION.

BY WARREN C. VOSBURGH.<sup>1</sup>

Received April 28, 1921.

It was pointed out by Nelson and Vosburgh<sup>2</sup> that a source of error about which little was known existed in the measurement of the velocity of hydrolysis of sucrose by invertase. The trouble was thought to consist in a change in activity which took place when invertase solutions were diluted, and the magnitude of the resulting error was found to vary with different invertase preparations. In some recent experiments an invertase preparation particularly subject to this error was used and as considerable accuracy in the experimental work was necessary for the purpose in view the results were of little value. An investigation was therefore undertaken of

<sup>1</sup> National Research Fellow.

<sup>2</sup> Nelson and Vosburgh, *THIS JOURNAL*, 39, 807 (1917).

the errors in the study of invertase action and a determination of how they may be reduced in magnitude.

### Experimental.

The procedure used in the above mentioned investigation was the following. An invertase and a sugar solution were prepared separately in concentrations twice those at which the invertase and sugar were desired in the finished solution. Equal volumes of the two were mixed to start the reaction and samples taken from time to time. Enough hydrochloric acid to bring the hydrogen-ion concentration to the desired value was usually included in the invertase solution. The most probable points in the procedure at which loss of activity might occur are where the solution containing the invertase is diluted. Therefore an invertase solution was diluted in different ways and the activities of the resulting solutions were compared.

**Dilution of Invertase with very Dilute Acid Solutions.**—The concentration of acid was so chosen that if the dilute invertase were mixed with an equal volume of a solution containing 20 g. of sucrose per 100 cc., but no buffer, the hydrogen-ion concentration of the resulting solution would be about  $4 \times 10^{-5} M$ . The hydrogen-ion concentration of the dilute invertase was therefore a little less than  $4 \times 10^{-5} M$ . Five cc. of the stock invertase was added to about 80 cc. of a solution containing the amount of acid or other substance shown in Col. 2 of Table 1, and the solution made up to 100 cc. A sugar solution was prepared containing 5 g. of sucrose, 21.9 cc. of water, or water containing some buffer. Both solutions were brought to the temperature of the thermostat,  $25^\circ \pm 0.01^\circ$ , 25 cc. of the dilute invertase was added to the sugar solution and the reaction allowed to proceed for exactly 2 hours. A 25-cc. sample was then run into 5 cc. of 0.01 molar sodium carbonate solution, and the optical rotation determined. The solutions at the start of the reaction all contained 5 g. of sucrose, 1.25 cc. of the stock invertase and 5 cc. of citrate and hydrochloric acid buffer solution<sup>3</sup> in 50 cc.<sup>4</sup> The hydrogen-ion concentration was determined colorimetrically<sup>5</sup> in each experiment, and varied only to a negligible extent in the various experiments. The results are shown in Table I.

It is shown in Table I that dilution of definite amounts of invertase with small amounts of various substances present gives solutions which vary in activity according to the substance present during dilution. Thus the presence of hydrochloric or sulfuric acid causes a noticeable loss in

<sup>3</sup> Buffer No. 1. See below.

<sup>4</sup> The small amount of acid in the dilute invertase and the alkali which was sometimes included in the sugar solution to neutralize it were considered negligible.

<sup>5</sup> The procedure was that used by Nelson and Vosburgh, *loc. cit.* The values are based on the assumption that the hydrogen-ion concentration of 0.1 *M* hydrochloric acid is 0.0920 *M*.

TABLE I.

Dilution of Invertase in the Presence of Various Substances.

The invertase solution was prepared by diluting 5 cc. of the stock solution with about 80 cc. of a solution containing substances noted in Col. 2, and making up to 100 cc. with water. 25 cc. was added to the sugar solution to start the reaction.

The sugar solution contained 5 g. sucrose, *a* cc. of solutions noted in Col. 3 and (21.9 — *a*) cc. of water.

A. Invertase No. 3.

Expt.	Invertase solution contains per 100 cc.	Sugar solution contains, <i>a</i> , cc. of buffer.	Conc. H <sup>+</sup> × 10 <sup>3</sup>	Rotation after 2 hrs.	Change in 2 hrs
9	a Water only	5	4.0	0.23	12.83
10		5	3.8	0.25	12.81
22	Water only	5	4.3	0.25	12.81
6	20 cc. buffer		4.1	0.52	12.54
7			3.8	0.32	12.74
8			3.8	0.32	12.74
26	10 cc. buffer	2.5	4.0	0.24	12.82
27		2.5	3.7	0.10	12.96
12	1.1 cc. 0.01 M HCl	5 <sup>b</sup>	3.9	0.95	12.11
13		5 <sup>b</sup>	3.7	1.11	11.95

B. Invertase No. 3A

40	Water only	5	4.1	0.34	12.72
45	Water only	5	4.3	0.32	12.74
46	1.0 cc. 0.005 M H <sub>2</sub> SO <sub>4</sub>	5	4.3	1.20	11.86
47		5 <sup>b</sup>	4.5	1.62	11.44
41	1.4 cc. 0.005 M Citric Acid	5 <sup>b</sup>	4.3	0.79	12.27
42		5	4.3	0.81	12.25
43	2.3 cc. 0.01 M Acetic Acid	5	4.3	0.56	12.50
44		5	4.5	0.60	12.46
48	1.1 cc. 0.005 M Tartaric Acid	5	4.3	1.06	12.00
49		5	4.3	1.00	12.06
52	0.059 g. NaCl	5	4.3	0.61	12.45
53		5	4.3	0.72	12.35

\* Brackets indicate that portions of the same dilute invertase solution were used in the experiments in the same bracket.

<sup>b</sup> Contains also 0.3 cc. of 0.01 N NaOH.

activity if the experiments in which the dilution is made with water only are taken as a standard. It is to be noted also that duplicate determinations in the case of dilution in the presence of hydrochloric or sulfuric acid agree poorly among themselves. Weak acids also cause losses in activity but duplicate determinations agree in this case. Different acids cause losses of different magnitudes.

The presence of a buffer causes a small loss in activity when all is included in the invertase solution and apparently a gain when half is in the invertase and half in the sugar. However, in both cases the results of duplicate

determinations do not agree well. It is strange that a citrate buffer in about 0.01 molar concentration should cause less loss in activity than citric acid at a much smaller concentration. Sodium chloride in 0.01 molar concentration acts much like citric acid.

**Reproducibility of Dilution with Water.**—The main conclusion to be drawn from Table I is that if an invertase solution is to be diluted with minimum loss in activity and in such a way that duplicate determinations of its activity will agree within less than 10 parts per thousand, the dilution must be made with pure water. The experiments listed in Table II show the degree of reproducibility of dilution with water. The procedure was like that of those experiments of Table I in which pure water was used for dilution of the invertase.

TABLE II.  
Reproducibility of Dilution with Water.

Five-cc. portions of invertase No. 3 were diluted to 100 cc. with water and 25 cc. added to a sugar solution containing 5 g. of sucrose, 16.9 cc. of water and 5 cc. of buffer No. 1.

Expt.	22.	23.	24.	25.	9.	35.	38.
Conc. $H^+ \times 10^6$ . . . . .	4.3	3.9	...	4.0	4.0	4.0	4.0
Rotation after 2 Hrs. . . . .	0.25	0.25	0.23	0.22	0.23	0.28	0.23
Change in 2 Hrs. . . . .	12.81	12.81	12.83	12.84	12.83	12.78	12.83

It is evident from Table II that in the dilution of invertase solutions with water duplication of results within 5 parts per thousand is possible. However dilution of 5 cc. of the stock solution to 100 cc. only is considered. Nelson and Hitchcock<sup>6</sup> have found that poor duplication resulted after a dilution considerably greater than this.

**Loss in Activity on Adding Invertase to a Sugar Solution.**—The total loss in activity before the beginning of the reaction must be the sum of the loss due to the preliminary dilution of the invertase and that taking place on mixing with the sugar solution. In drawing the conclusions above it has been assumed that the second loss is either constant or small compared with the first. It seems reasonable to conclude from Table II that if the presence of a citrate buffer has any effect at this point the effect is reproducible within at most 5 parts per thousand and therefore that the above assumption is justified. The effect of some other sources of hydrogen ion when used instead of the buffer is shown in Table III. The experiments were carried out according to the same procedure as those of Table I, the invertase being diluted with water only and the substances noted in Col. 2 being present in the respective sugar solutions.

In the experiments of Table III the differences in the change in rotation can be ascribed to changes in the activity of the invertase at the time of mixing with the sugar solution or to different rates of reaction. The

<sup>6</sup> Private communication



TABLE III.

Effect of Various Sources of Hydrogen Ion when Included in the Sugar Solution Previous to Adding the Invertase.

Invertase solution : 5 cc. of Invertase 3 A per 100 cc. diluted with water only.

Sugar solution : 5 g. of sucrose, (21.9—*a*) cc. of water and *a* cc. of solution in Col. 3.

Expt.	Sugar solution contains, Cc.	Solution.	Conc. H <sup>+</sup> × 10 <sup>5</sup>	Rotation after 2 hrs.	Change in 2 hrs.
45	5	Buffer No. 1	4.3	0.32	12.74
70	5	" " 1	4.0	0.31	12.76
64	0.25	0.01 <i>M</i> HCl	2.8	0.37	12.70
65	0.25	0.01 <i>M</i> HCl	3.8	0.42	12.65
66	0.25	0.005 <i>M</i> H <sub>2</sub> SO <sub>4</sub>	3.6	0.40	12.67
67	0.25	0.005 <i>M</i> H <sub>2</sub> SO <sub>4</sub>	4.0	0.39	12.68
68	0.35	0.005 <i>M</i> Citric Acid	3.5	0.45	12.62
69	0.35	0.005 <i>M</i> Citric Acid	3.7	0.49	12.58
73	0.6	0.01 <i>M</i> Acetic Acid	3.5	0.59	12.48
74	0.6	0.01 <i>M</i> Acetic Acid	3.5	0.59	12.48
75	0.3	0.005 <i>M</i> Tartaric Acid	3.7	0.74	12.33
76	0.3	0.005 <i>M</i> Tartaric Acid	3.5	0.70	12.37

latter explanation seems less probable. Retardation similar to that found by Fales and Nelson<sup>7</sup> to be caused by sodium chloride cannot have taken place since the concentrations of electrolyte were small, the hydrogen-ion concentration was the optimum, and the largest concentration of electrolyte was present in the experiment in which the fastest reaction took place. Since dilution of the stock invertase with very weak electrolyte solutions is attended by a loss in activity it is reasonable to expect that dilution of an invertase solution with a sugar solution containing the same electrolyte would also be attended by a loss in activity. Therefore it is assumed that the differences in reaction velocity in the various experiments were chiefly due to changes in activity of the invertase on mixing with the sugar solution.

The results of dilution with a sugar solution containing various sources of hydrogen ion are similar to the results of dilution of the stock invertase with water containing the same substances. A greater loss in activity takes place when free acids are the source of hydrogen ion than when a buffer is used. However the loss in activity caused by the strong acids is here less than that caused by the weak ones. The magnitude of the losses is in most cases much smaller than those in the experiments of Table I. This might be explained as due to the smaller amount of dilution, 25 cc. to 50 cc. as compared with 5 to 100, or it might be explained as the result of "protective action"<sup>8</sup> of the sugar.

<sup>7</sup> Fales and Nelson, *THIS JOURNAL*, 37, 2769 (1915).

<sup>8</sup> O'Sullivan and Thompson, *J. Chem. Soc.*, 57, 900 (1890), have shown that sucrose protects invertase from destruction by hot water; and Hudson, *THIS JOURNAL*, 32, 988, 1354 (1910) has shown that fructose also protects it from destruction by hot water as well as by acids and alkalies, and that sucrose protects it from destruction by alcohol.

That sucrose has such a protective action in this case is shown in the experiments of Table IV. In these, 5 cc. of the stock invertase was added directly to 195 cc. of a solution containing 20 g. of sucrose, and either 20 cc. of buffer or the quantity of acid necessary to make the hydrogen-ion concentration of the completed solution about  $4 \times 10^{-5} M$ . The concentrations of invertase, sucrose, and hydrogen ions are consequently the same as in the experiments of Table III, only the total volume and manner of mixing differing.

TABLE IV.

Rate of Hydrolysis when No Preliminary Dilution is Made.

The sugar solution contained 20 g. of sucrose, (182.6 — *a*) cc. of water and *a* cc. of acid or buffer as noted in Col. 3. 5 cc. of Invertase 3 A was added.

Expt.	Sugar solution contains, Cc.	Solution.	Conc. $H^+$ $\times 10^5$ .	Rotation after 2 hrs.	Change in 2 hrs.
60	20	Buffer No. 1	4.0	0.17	12.89
61	20	Buffer No. 1	4.1	0.17	12.89
78	20	Acetate Buffer	4.3	0.22	12.84
83	20	Acetate Buffer	4.1	0.29	12.77
87	1.4	0.005 <i>M</i> $H_2SO_4$	4.7	0.45	12.61
80	2.3	0.005 <i>M</i> Citric Acid	4.4	0.42	12.64
86	2.1	0.005 <i>M</i> Citric Acid	5.1	0.39	12.67
81	4.8	0.01 <i>M</i> Acetic Acid	5.5	0.39	12.67
84	4.3	0.01 <i>M</i> Acetic Acid	5.1	0.45	12.61

The results given in Table IV are similar to those in Table III. Dilution with a sugar solution containing a very weak electrolyte evidently has less destructive action than dilution with a very weak electrolyte in absence of sugar. Expts. 60 and 61 as compared with Expts. 45 and 70 in Table III show that in the latter there is a loss in activity on dilution of the invertase with water.

It seems reasonable that the best procedure to adopt in the study of invertase action is that which will give the fastest reaction, other conditions being the same. The experiments of Tables III and IV point out therefore that the invertase should be used without preliminary dilution if possible, and that buffers are preferable to acids as the source of hydrogen ions.

**Experiments with Other Invertase Preparations.**—Experiments similar to some of the above experiments were carried out with two other invertase preparations, Nos. 2 and 8, and the results are given in Tables V, VI, and VII. The procedure was essentially the same as in the experiments of Tables I, III and IV respectively.

It is shown in Table V that dilution in presence of hydrochloric acid has some destructive action on Invertases 8 and 2 but the amount is noticeably less than that in the case of Invertase 3. In case of Invertase 2 it is probable that the amount of acid used was not equal with respect to the dilution effect to that used with Invertases 3 and 8, since more

TABLE V.

Dilution of Invertase Preparations 2 and 8 with Very Weak Acid Solutions.

Procedure as in experiments of Table I. Sugar solutions contained 5 g. of sucrose, 16.9 cc. of water and 5 cc. of buffer.

A. Invertase No. 8.

Expt.	Invertase solution contains per 100 cc. Cc. Solution.		Buffer No. <sup>b</sup> .	Conc. H <sup>+</sup> × 10 <sup>4</sup> .	Rotation after 2 hrs.	Change in 2 hrs.
90	0.8	0.01 M HCl	1	3.8	-1.09	14.14
96			2	4.4	-1.07	14.12
98			2	4.5	-1.07	14.12
122			3	4.5	-1.10	14.15
91			1	4.5	-1.00	14.05
92	1.1	0.01 M HCl <sup>a</sup>	1	4.3	-1.01	14.06
101			2	4.0	-0.74	13.79
124			3	4.3	-0.82	13.87

B. Invertase No. 2. 10 cc. of stock solution per 100 cc. of dilute invertase.

125			3	4.3	4.79	8.33
132			3	4.7	4.84	8.28
138			3	4.5	4.85	8.27
127	1.1	0.01 M HCl <sup>a</sup>	3	4.3	4.85	8.27
135	1.1	0.01 M HCl <sup>a</sup>	3	4.3	4.87	8.25

<sup>a</sup> Sugar solution contained 0.3 cc. of 0.01 M NaOH, 16.6 cc. of water and 5 cc. of buffer to 5 g. of sucrose.

<sup>b</sup> Citrate and hydrochloric acid buffers.

acid was required to bring a solution containing Invertase 2 in the concentration used to a hydrogen-ion concentration of  $4 \times 10^{-5} M$  than in the case of Invertases 3 and 8. The magnitude of the dilution effect on Invertase 8 seems to be somewhat dependent on the hydrogen-ion concentration, the loss in activity being larger when the acid concentration is larger. Therefore although the observed loss in activity by Invertase 2 is small, it probably would be somewhat larger if an amount of acid equivalent to that in the experiments with Invertase 8 were present.

It can be concluded from Table V that dilution of any invertase in presence of hydrochloric acid is likely to result in loss in activity, but that the magnitude of the losses under the same conditions differs in different invertase preparations. Invertase solutions may be classified according to stability, the more stable ones being those like Nos. 2 and 8 which lose the least on dilution and the less stable being those like No. 3. Dilution with water is reproducible within 2 parts per thousand in the case of Invertases 8 and 2.<sup>9</sup>

<sup>9</sup> The rather large difference between Expts. 125 and 132 with Invertase 2 may have been due to decrease in activity of the stock solution during the 11 days which elapsed between the two experiments, the solution having been removed from the ice-box during part of 1 day. In view of this the experiments with Invertase 2 numbered above 128 should be compared with No. 128 rather than with No. 125, and those numbered below 125 should be compared with the latter.

TABLE VI.

Effect on Invertases 2 and 8 of Acids when Present in the Sugar Solution Previous to Adding the Invertase.

Procedure as in the experiments of Table III except that a 10-cc. portion of Invertase 2 was used.

## A. Invertase No. 8.

Expt.	Sugar solution contains,		Conc. H <sup>+</sup> × 10 <sup>3</sup> .	Rotation after 2 hrs.	Change in 2 hrs.
	Cc.	Solution.			
90	5	Buffer No. 1	3.8	-1.09	14.14
96	5	Buffer No. 2	4.4	-1.07	14.12
93	0.25	0.01 M HCl	3.4	-1.03	14.08
97	0.27	0.01 M HCl	3.6	-1.07	14.12
123	0.30	0.01 M HCl	5.0	-1.00	14.05
99	0.38	0.005 M Citric Acid	3.7	-1.05	14.10
100	0.38	0.005 M Citric Acid	3.7	-1.05	14.10

## B. Invertase No. 2.

125 <sup>a</sup>	5	Buffer No. 3	4.3	4.79	8.33
132	5	Buffer No. 3	3.7	4.84	8.28
138	5	Buffer No. 3	4.5	4.85	8.27
126	0.35	0.01 M HCl	3.7	4.91	8.21
139	0.37	0.01 M HCl	4.2	4.94	8.18
140	0.52	0.005 M Citric Acid	4.3	4.86	8.26
141	0.52	0.005 M Citric Acid	4.4	4.87	8.25

<sup>a</sup> See note above.

Table VI shows that the conclusions drawn from Table III can be extended to apply to other invertase preparations, except as to the magnitude of the losses in activity under the various conditions. The change in rotation in the experiments with citric acid as the source of hydrogen ions is only 2 to 3 parts per thousand less than in the experiments in which buffer is used. With the more stable invertase preparations therefore citric acid can be used as the source of hydrogen ions instead of a buffer. Hydrochloric acid is less reliable as to reproducibility and should not be used when results of high precision are desired.

TABLE VII.

Rate of Hydrolysis when No Preliminary Dilution is Made.

The procedure was like that of the experiments of Table IV. Five cc. of invertase was used in each experiment.

Expt.	Invertase No.	Buffer No.	Cc.	Sucrose. G.	Water. Cc.	Conc. H <sup>+</sup> × 10 <sup>3</sup> .	Rotation after 2 hrs.	Change in 2 hrs.
105	8	2	20	20	162.6	4.3	-1.11	14.16
106	8	2	20	20	162.6	4.6	-1.11	14.16
136	2	3	10	10	78.8	4.3	4.82	8.30
137	2	3	10	10	78.8	4.3	4.83	8.29

Comparison of the experiments in Table VII in which no preliminary dilution was made with those of Table V in which preliminary dilution was

made shows that in the case of Invertases 8 and 2 only small losses in activity took place on dilution with water, the change in rotation being about 3 parts per thousand<sup>10</sup> larger than in the case in which no preliminary dilution was made. The difference between stable and unstable invertase preparations is noticeable in the amount of loss in activity caused by dilution with distilled water.

**Loss in Activity by Dilute Invertase on Standing.**—In the above experiments the dilute invertase solutions were used within 2 hours after preparation. It was found that such solutions when kept at 25° lost activity as time went on. For example in an experiment with Invertase 3A the change in rotation using the freshly prepared dilute invertase was 12.78°, while that after the solution had been kept for one day was 12.69°. The activity decreased regularly and after 11 days the change in rotation was 12.38°. When a similar solution was kept in the ice-box the loss in activity was much slower, but still appreciable. In this case the change in rotation when the invertase was freshly diluted was 12.48° and after 20 days was 12.35°.

A similar loss in activity takes place in dilute solutions of other invertase preparations. In the case of the dilute Invertase 8 used in Expt. 96<sup>11</sup> determinations after 1 and 4 days' standing at 25° gave respectively 13.98° and 13.82° change in rotation as compared with 14.12° in Expt. 96. The dilute Invertase 8 used in Expt. 122<sup>11</sup> was kept in the ice-box for 12 days after which the change in rotation was 13.99° as compared with 14.15° in Expt. 122. In the case of Invertase 2 the dilute solution of Expt. 138, giving in that experiment a change in rotation of 8.27° gave after 5 days in the ice-box 8.03°.

Hudson and Paine<sup>12</sup> claim that destruction of invertase by acids or alkalis is only appreciable when the acid or alkali concentration is 0.01 molar or greater. The hydrogen-ion concentration of a dilute solution of Invertase 3A was found to be 5.77 when freshly diluted, and after 5 days 5.84. This would indicate that the loss in activity is due to some other cause than the destructive action of acids or alkalis. On the other hand when a small amount of acid was present in the dilute invertase it was found that the loss in activity in two days was much greater than the loss during the same time by a solution made up without acid.

**Loss in Activity by Stock Solutions.**—Fales and Nelson<sup>7</sup> reported that the stock solution used by them did not lose in activity to an appreciable extent in a year. However, the above results for the dilute invertase suggest that the stock solutions may have lost in activity also. In Table

<sup>10</sup> Expts. 105 and 106 are compared with 96 and 98 since the same buffer was used in all.

<sup>11</sup> Table V.

<sup>12</sup> Hudson and Paine, *THIS JOURNAL*, 32, 774 (1910).

VIII are collected the results of several experiments on the activity of Invertases 3A and 8 over a period of more than 3 months. The procedure in these experiments was like that of the experiments of Table II. It is shown that these stock solutions lose slowly in activity. The more stable invertase preparations change more slowly than the less stable ones. The decrease in activity in Invertase 3A is a little more than half the rate at which the dilute solution which was kept in the ice-box changed. In the case of Invertase 8 the stock solution changed much more slowly than the dilute solution.

TABLE VIII.

Activity of Stock Invertase Solutions.

Procedure as given in Table II.

Expt.	Invertase.	Date.	Buffer. No.	Conc. H <sup>+</sup> × 10 <sup>4</sup> .	Rotation. after 2 hrs.	Change. in 2 hrs.
40	3 A	Aug 2	1	4.1	0.34	12.72
54	3 A	" 5	1	3.9	0.29	12.77
70	3 A	" 10	1	4.0	0.31	12.76
118	3 A	" 26	3	4.3	0.41	12.66
149	3 A	Oct. 13	3	4.1	0.63	12.44
151	3 A	Nov. 18	3	4.5	0.76	12.31
90	8	Aug. 18	1	3.8	-1.09	14.14
122	8	" 27	3	4.5	-1.10	14.15
150	8	Oct. 13	3	4.1	-1.02	14.07
152	8	Nov. 18	3	4.3	-0.98	14.03

In using an invertase solution care should be taken to make a complete series of experiments in as short a time as possible and to measure the activity of the invertase at least at the beginning and end of the series if the series is long. Furthermore, considering also the previous action, it follows that if it is necessary to dilute a stock solution, it should be freshly diluted just previous to using.

In making up Tables I to VII only the results of experiments with any one invertase which were made within such time limits that the deterioration meanwhile was negligible were included in any one section of a table.

### Experimental Details.

**Measurement of the Initial Rotation.**—In using invertase inactivated by boiling to make blank determinations of the initial rotation the assumption is made that boiled invertase has practically the same specific rotation as the active invertase. Therefore the optical rotation was determined of boiled and unboiled portions of the invertase preparations used in this investigation. Five-cc. portions of Invertases 3A and 8 and a 10-cc. portion of Invertase 2 were made up to 100 cc. with water. Twenty-five-cc. samples were taken and run into 25 cc. of water and 10 cc. of 0.01 *M* sodium carbonate solution, this procedure being similar to that of the actual experiments except that the sugar was omitted. A portion of the 100 cc. of dilute invertase solution was brought to the boiling point and allowed to cool and the sampling repeated. The optical rotations of the solutions so prepared were determined, and found to be 0.05, 0.02 and 0.12 for the active Invertases 3A, 8 and 2 respectively, and 0.05, 0.03, 0.12 for the inactive

invertases, respectively. Invertase inactivated by boiling evidently has for practical purposes the same specific rotation as active invertase. It is also shown that a separate blank determination must be made for each invertase preparation.

Blank determinations to apply to the above experiments were made as follows. Sugar solutions were prepared containing 5 g. of sucrose and 21.9 cc. of water, or water and buffer as noted below. Five-cc. portions of Invertases 3A and 8 or 10-cc. portions of Invertase 2 were diluted with water and heated to boiling. The invertase solutions were allowed to cool, made up to 100 cc. and 25-cc. portions were added to the sugar solutions as in the actual experiments. Twenty-five-cc. samples were then run into 5-cc. portions of 0.1 *M* sodium carbonate solution and the optical rotations determined. In the experiments using Invertase 3A two different sucrose preparations were used, the first in Expts. 6 to 52 and the second in the experiments numbered higher than 52. Blank determinations of the initial rotation were made for Invertase 3A with both. The second sucrose preparation was used in the experiments with the other invertase preparations. The initial rotations were as follows:

A. Invertase 3A.

Sucrose No.....	1	1	1	1	2	2
Buffer, cc.....	5	5	..	...	5	5
0.005 <i>M</i> H <sub>2</sub> SO <sub>4</sub> , cc. ...	...	...	0.3	0.3	...	...
Rotation.....	13.06	13.06	13.06	13.07	13.07	13.07

B. Invertase 8.

Rotation.....	13.05	13.05
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C. Invertase 2.

Rotation.....	13.12	13.13
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The initial rotation for the experiments like those of Table IV was determined for Invertase 3A using the same procedure as in actual experiments but with inactive invertase. It was found to be 13.06° which is 0.01° lower than with the above procedure. Since 0.01° is about the limit of accuracy in reading the polariscope the initial rotations in the case of the experiments of Table VII were taken as the same as those given in B and C above.

**Determination of the Change in Rotation.**—The invertase solution was added to the sugar solution by means of a calibrated pipet and the time of the start of the reaction considered as the mean time of delivery. The reaction was allowed to proceed for 2 hours and then a 25-cc. sample was withdrawn and run into 5-cc. of 0.01 *M* sodium carbonate solution<sup>13</sup> at a time such that the mean time of delivery would be exactly 2 hours after the start of the reaction. The rotation of the sample was determined after at least 10 minutes and before it had stood 2 hours, by means of a Schmidt and Haensch polariscope which could be set and read to about 0.01°. Light from a mercury-vapor lamp filtered by a Wratten No. 74 filter was used for the polariscopic measurements. The temperature of the sample was maintained at 25° during the determination of the rotation by means of the thermostat described by Nelson and Beegle.<sup>14</sup> The zero point of the polariscope was determined at least once on each day on which determinations were made, using one of the polariscope tubes filled with distilled water. The cover glasses were tested occasionally by turning the tubes while making readings but no optical rotation was ever observed in the 4 cover glasses used throughout this investigation.

**Preparation of the Invertase.**—Invertase 3 and Invertase 8 were prepared in this laboratory by Mr. D. I. Hitchcock and Invertase 2 by Dr. H. L. Simons, the author being indebted to both for the invertase used in this investigation. Nos. 2 and 3 were prepared from autolysed yeast which had been standing for several years. No. 8 was

<sup>13</sup> Hudson, *THIS JOURNAL*, 30, 1564 (1908).

<sup>14</sup> Nelson and Beegle, *ibid.*, 41, 559 (1919).

prepared from fresh yeast. Autolysis, precipitation of the proteins and dialysis were carried out as described by Nelson and Born.<sup>15</sup> The invertase was however not precipitated from the dialyzed solutions, the latter being used as the "stock solutions." Invertase 3A was a small portion of Invertase 3 which was removed and kept in a smaller bottle for convenience. The apparent difference in activity between the two may have been due to deterioration during the time that elapsed between the experiments with Invertase 3 and those with 3A. All stock solutions were kept in an ice-box.

**Preparation of the Sucrose.**—Rock candy known to have been made from the best commercial sucrose was dissolved and reprecipitated by addition of alcohol as described by Cohen and Commelin.<sup>16</sup> It was dried over conc. sulfuric acid at about 50° and preserved in glass-stoppered bottles sealed with paraffin.

**Preparation of the Buffers.**—Buffers 1 and 3 were prepared by adding 197 cc. of 0.1 *M* hydrochloric acid to 303 cc. of secondary sodium citrate freshly prepared as described by Sorensen.<sup>17</sup> Buffer No. 2 was prepared similarly using a citrate solution prepared from *N* sodium hydroxide solution which had stood for some time and had dissolved some silica from the bottle. The acetate buffer was prepared by adding 655 cc. of 0.1 *M* acetic acid to 345 cc. of 0.1 *N* sodium acetate.

Experiments similar to those of Table II with Invertase 3A using the different buffer solutions are shown in Table IX. The slight amount of impurity in buffer No. 2 was found to have an appreciable effect on the velocity of hydrolysis. Expts. 117 and 118 show that the velocity when buffer No. 2 is used is less than when No. 3 is used. The apparent difference between the effects of Buffers 1 and 3 on the velocity of hydrolysis can be explained by deterioration of the invertase during the time between Expts. 70 and 118.

The acetate buffer gives a velocity of hydrolysis which is a little less than that when a citrate buffer is used as Expts. 70, 71 and 72 in Table IX and 60, 61, 78 and 83 in Table IV show.

TABLE IX.

Effect of Different Buffers on the Activity of Invertase.

Procedure as in the experiments of Table II.

Expt.	Buffer.	Date, Aug.	Conc. H <sup>+</sup> × 10 <sup>3</sup> .	Rotation after 2 hrs.	Change in 2 hrs.
40	Citrate No. 1	2	4.1	0.34	12.72
70		10	4.0	0.31	12.76
95		19	3.8	0.52	12.55
107		23	4.3	0.49	12.58
117		26	4.3	0.59	12.48
118	Acetate	26	4.3	0.41	12.66
71		10	4.3	0.40	12.67
72		10	4.5	0.36	12.71

The differences in the effect of the different citrate buffers on Invertase 8 are shown in Table V to be very small. Here again the difference between a stable and an unstable invertase preparation is noticeable, the former being preferable.

### Summary.

1. Invertase solutions are subject to loss in activity when diluted. The loss varies with the substances present in the water with which the invertase is diluted.

<sup>15</sup> Nelson and Born, *THIS JOURNAL*, 36, 393 (1914).

<sup>16</sup> Cohen and Commelin, *Z. physik. Chem.*, 64, 1 (1908).

<sup>17</sup> Sorensen, *Biochem. Z.*, 21, 131 (1909).



2. Dilution with distilled water is attended by less loss than is the case in dilution with very weak acids, and is reproducible for practical purposes if the dilution is not too great.

3. When an invertase solution is added to a solution containing sucrose, losses in activity due to dilution are less than when the invertase is diluted by a similar solution not containing sucrose.

4. The velocity of hydrolysis of sucrose by invertase is greater when a citrate buffer or acetate buffer is used as the source of hydrogen ions than when citric or acetic acid respectively is so used.

5. With different invertase preparations the magnitude of the losses in activity on dilution varies. Invertase solutions may be designated as more or less stable according to the magnitude of such losses in activity.

6. Both dilute and stock solutions of invertase lose strength on standing, the former faster than the latter. Stock solutions of the more stable invertase preparations lose activity more slowly than stock solutions of the less stable invertase preparations.

NEW YORK, N. Y.

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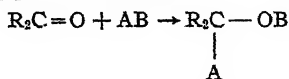
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

## ADDITION REACTIONS OF THE CARBONYL GROUP INVOLVING THE INCREASE IN VALENCE OF A SINGLE ATOM.

By JAMES B. CONANT.

Received April 29, 1921.

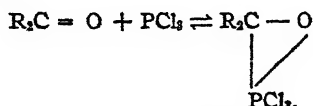
The addition reactions of the phosphorus halides, which have been described in previous papers,<sup>1</sup> are of a different type from the usual addition reactions of simple or conjugated carbonyl compounds. They involve the formation of a cyclic compound by reason of the increase in valence of a single atom, while in most addition reactions of carbonyl compounds the reagent seems to have dissociated into two parts which subsequently become attached to the carbon and oxygen atoms. The Grignard reagent, hydrocyanic acid, and sodium bisulfite may be mentioned as common examples of this usual type of reaction.



These common reagents react with  $\alpha,\beta$  unsaturated ketones and aldehydes in much the same manner. When they combine with the conjugated system, the two parts of the addendum attach themselves in the 1,4 position to the oxygen and carbon atoms. The molecule of the reagent apparently undergoes cleavage into the same fragments in the case of both 1,2 and 1,4 additions.

<sup>1</sup> THIS JOURNAL, 39, 2679 (1917); 42, 830, 2337 (1920); 43, 1665, 1667 (1921).

The 1,4 addition of phosphenyl chloride and the 1,2 and 1,4 additions of phosphorus trichloride do not fit into this classification; they seem to be examples of another sort of addition reaction. In these cases the addendum unites with the carbonyl group or conjugated system *without cleavage* and the phosphorus atom increases its apparent valence by two. The reaction is reversible.



Such reactions involving the increase in valence of a single atom have been found to take place with a variety of simple carbonyl compounds, and also with unsaturated ketones. The phosphorus halide, also, may be varied. As shown in the experimental portion of this article, phosphorus tribromide readily adds in the 1,4 position to benzal-acetophenone. The equilibrium is more in favor of the addition product than with the trichloride. Several instances of the 1,4 addition of phosphenyl chloride have already been investigated and unpublished results obtained in this laboratory have shown that diphenoxy-chlorophosphine, monophenoxy-dichlorophosphine and diethoxy-dichlorophosphine behave in a similar manner. The reaction is thus general enough to warrant consideration from a theoretical standpoint.

Reactions of this special type are common in inorganic chemistry; for example, the reaction between ammonia and the halogen acids or between the trivalent phosphorus halides and chlorine. These reactions take place with the increase of valence of a single atom, and are for the most part reversible. The work of Werner and others provided a starting point for an interpretation of pentavalent nitrogen compounds, and the theory of the cubical atom as developed by G. N. Lewis<sup>2</sup> and later by Langmuir<sup>3</sup> has provided a satisfactory picture of the changes of valence of the elements in the fifth group of the periodic table. An application of this view has been helpful in the investigations just discussed and a further expansion of it leads to a general hypothesis in regard to most reactions of carbonyl compounds.

### The Change from a Covalence of Three to a Covalence of Four.

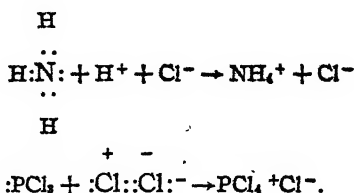
According to Lewis' theory the three hydrogen atoms in ammonia are held to the nitrogen by the sharing of pairs of electrons of a group of eight. In ammonium chloride the four hydrogen atoms are likewise held by the sharing of electrons but the chlorine atom is not directly bound to the nitrogen; it is a negatively charged atom, and in solid ammonium chloride is held with the positively charged ammonium radical in a certain

<sup>2</sup> Lewis, *THIS JOURNAL*, 38, 762 (1916).

<sup>3</sup> Langmuir, *ibid.*, 41, 868 (1919).

spatial arrangement by electrostatic forces. In solution both ions are free to move about. The linkage of hydrogen to nitrogen is a non-polar bond, (usually referred to as valence in organic chemistry); the chlorine atom is held by a polar bond (what is usually meant by valence in the chemistry of electrolytes). Similarly it seems probable that in phosphorus pentachloride, four chlorine atoms are held by non-polar bonds, and one by a polar bond. This is often represented thus:  $[(\text{PCl}_4) + \text{Cl}^-]$ .

The mechanism by which the non-polar valence (the covalence) of nitrogen and phosphorus in such compounds increases from three to four has been but little discussed. It involves the attachment of a positively charged atom or group by means of the two unshared electrons of the tri-valent atom. In aqueous solution it is probably the hydrogen ion which is thus attracted. To explain the reaction in non-aqueous solutions or the addition of such non-electrolytes as methyl iodide to  $\text{RNH}_2$  or chlorine phosphorus trichloride, one may either posit the existence of ions, or conceive of molecules in which one pair of electrons is pulled toward one atom to such an extent that the positive nucleus of the other is exposed. Lewis<sup>2</sup> has already pointed out these alternatives in the case of the halogens; there is some evidence which points to the existence of positive and negative halogen ions. Until more is known about this "ionization" of essentially non-polar substances no clear line can be drawn between the two cases. The addition reactions of inorganic chemistry, of the type under consideration, seem to depend on the attraction of the positive nucleus of some ion or "partially ionized" molecule, and the resulting formation of a polar compound;



From the same point of view the carbon atom of the carbonyl group may act as if it were a positively charged ion. The positive nucleus of the carbon atom is more exposed in such compounds than in saturated compounds because of the drawing away of the two electrons which are shared with the oxygen octet. The *positively charged nucleus* will attract the unshared electrons of the central atom of such compounds as ammonia or phosphorus trichloride. When the molecules are drawn sufficiently close together an addition compound will be formed. The oxygen atom of this compound will be negatively charged, the nitrogen or phosphorus atom positively charged. The polar bond corresponding to the chloride ion of ammonium chloride will then be an "inner polar bond" such as exists in the amino acids;

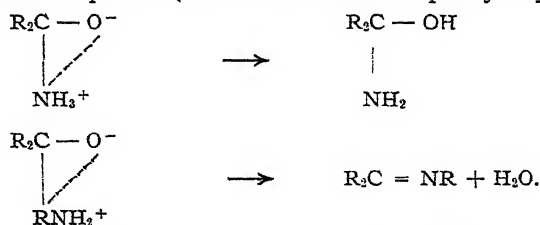


transformed<sup>4</sup> to  $R_2CHOHPO(OH)_2$ . Similarly, as described in earlier papers, the 1,4 addition compound reacts with acetic anhydride producing a cyclic anhydride; with acetic acid an open chain phosphonic acid is formed.

This great reactivity of the chlorine atoms attached to the pentavalent phosphorus atom of the addition compound, is of great practical importance in carrying out all these addition reactions. It is possible to cause the reversible addition reactions to go to completion if cold acetic acid or acetic anhydride is used as a medium; if the proper temperature is maintained only the addition product will act with the acetic acid or anhydride. Very good yields of phosphonic acids (or their cyclic anhydrides) can thus be obtained from equimolecular amounts of phosphorus halide and unsaturated compound. However, in the initial addition reaction only about 30% of the two substances have combined as can be shown by rapidly decomposing the mixture with water, (see experimental part).

### Reactions of Nitrogen Compounds.

In the case of the addition compounds of aldehydes with ammonia and substituted ammonias, such as hydroxylamine and phenylhydrazine, the initial product cannot rearrange in the same manner as the phosphorus trichloride addition product. Such a rearrangement would involve the formation of a negative hydrogen ion, which is obviously impossible. Rearrangement may take place, however, so that a hydrogen atom shifts to the oxygen atom, or water may be eliminated from the molecule forming an unsaturated compound (such as an oxime or phenyl hydrazone);



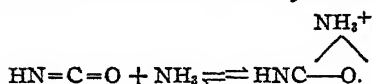
If neither of these possibilities can occur no stable addition product can be isolated as the initial reaction is easily reversible, and stops at some equilibrium point. However, in certain cases it may be that a compound of the inner salt type can be stable without rearrangement. E. A. Werner,<sup>5</sup>

or example, believes the formula for urea to be  $NH = \overset{\overset{O^-}{\diagup}}{\underset{\diagdown}{C}} NH_3^+$  and

<sup>4</sup> THIS JOURNAL, 42, 2337 (1920).

<sup>5</sup> Werner, *J. Chem. Soc.*, 113, 84 (1918).

writes the reaction for its formation from cyanic acid and ammonia as

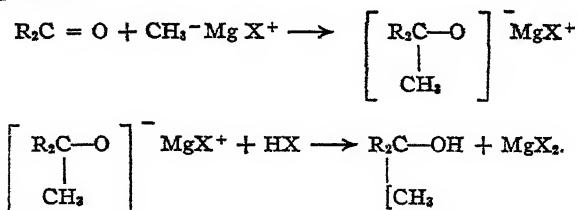


This is, of course, exactly the type of reaction we are here considering, and if Werner is correct in the interpretation of his experiments, the addition of ammonia to cyanic acid is another case of an addition reaction of a carbonyl group which involves the increase in covalence of the addendum.

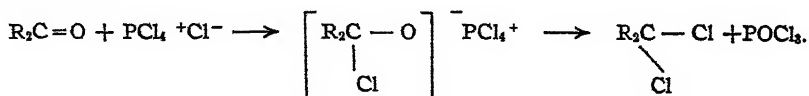
From this point of view, the great reactivity of trivalent nitrogen compounds towards aldehydes and ketones is due to the *attraction of the unshared pair of electrons on the nitrogen atom by the "exposed" nucleus of the carbon atom of the carbonyl group*. It is exactly this attraction of the unshared electrons by the positive nucleus of the hydrogen ion which makes these same compounds weak bases. The two phenomena are thus parallel.

### The Hypothesis Applied to Other Reactions.

Many reactions which do not seem to involve the increase in valence of a single atom may also be interpreted by this hypothesis. Recent investigations<sup>6</sup> seem to indicate that the Grignard reagent acts as if it were at least partially ionized; for example, into  $\text{CH}_3^-$  and  $\text{MgI}^+$ . Such a negative ion would be attracted by the positive carbon atom of the carbonyl group; the product would be the salt of a very weak acid (the carbinol) which on treatment with water or acid would yield the hydrogen compound;



Phosphorus pentachloride is another somewhat different reagent. Here the negative chlorine is attracted and the positive  $\text{PCl}_4$  group is held to the resulting complex by a polar bond. Such a compound might undergo an irreversible intramolecular change with the formation of  $\text{POCl}_3$  and a dichloride;

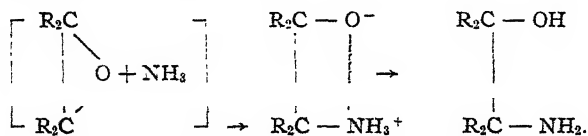


<sup>6</sup> THIS JOURNAL, 39, 82 (1917).



equilibrium of the initial reaction but on the speeds of the subsequent reactions. By analogy with certain inorganic substances and reactions it has been possible to formulate roughly some of these factors in the case of the action of the phosphorus halides. Until more quantitative evidence is at hand it will not be profitable to discuss the influence of various groups on the course of such reactions, although eventually this hypothesis should be useful in correlating many of the facts concerning the so-called "reactivity" of carbonyl compounds.

The reactions of ethylene oxides<sup>7</sup> are readily formulated by means of this same hypothesis. The electrons of the carbon atoms are drawn away in the formation of a three-membered ring leaving the positive nucleus of the carbon atoms exposed. The force fields of these carbon nuclei would attract the same sort of molecules as in the case of carbonyl compounds. The resulting substances could undergo the same sort of rearrangement; for example with ammonia;



This electronic interpretation of the facts summarized by Baeyer's strain theory has already been pointed out by Langmuir. In larger rings the electrons are drawn away to a less extent and four-, five- and six-membered rings are therefore less reactive.

In conclusion the writer wishes to express his great indebtedness to Dr. E. Q. Adams of the Bureau of Chemistry for having pointed out to him in 1917 the possibility of applying Professor Lewis' ideas to the addition reactions of phosphorus trichloride and to similar problems in organic chemistry.

### Experimental.

**The Equilibrium between Phosphorus Trichloride and Benzal-acetophenone.**—The addition reaction between benzaldehyde and phosphorus trichloride has already been shown<sup>8</sup> to be reversible; a definite equilibrium point is reached and the determination of this equilibrium has shown that the reaction follows the usual law of mass action. The method used in that case was to decompose the reaction mixture with water and determine the amount of phosphorus acid formed by the hydrolysis of the uncombined trichloride. Both the addition product and the trichloride react so rapidly with water that little if any shifting of the equilibrium takes place during hydrolysis. The results obtained showed that when

<sup>7</sup> The action of the phosphorus halides on such compounds is being investigated.

<sup>8</sup> *THIS JOURNAL*, 42, 2337 (1920).



equimolecular amounts of benzaldehyde and phosphorus trichloride are brought together, equilibrium is obtained when 30% of the material has combined.

It was of interest to obtain some similar values for the 1,4 addition of phosphorus trichloride. This was done in a rough way by determining the amount of phosphonic acid formed (which is insoluble in water) and the amount of ketone left unchanged when the reaction mixture was decomposed with water. The procedure was as follows.

Five g. of benzal-acetophenone, 0.024 g. mol. (carefully dried in a vacuum over phosphorus pentoxide), and 3.4 g. of phosphorus trichloride (0.025 g. mol.) were mixed together in a glass tube which was then sealed. The solid ketone soon dissolved almost completely in the trichloride. The mixture was allowed to stand for a definite time at room temperature (25°). The tube was then opened and the contents quickly stirred into 250 cc. of water. The water solution was carefully extracted with ether and the phosphonic acid then removed from the ethereal layer by extraction with sodium hydroxide. Evaporation of the ether yielded the unchanged ketone. The phosphonic acid was obtained by acidifying the sodium hydroxide solution and extracting with ether. The amount of recovered ketone and phosphonic acid in every case accounted for at least 95% of the original material. The following results were obtained.

Hours.	Acid g.	Ketone equivalent.	Per cent. reacted.
1	1.5	1.1	22
2	1.6	1.2	24
3	1.5	1.1	22
1 (4 mols $\text{PCl}_3$ )	3.2	2.3	46

These figures while only approximate show that the reaction comes to a definite equilibrium in a comparatively short time. When a large excess of one of the materials is employed (last experiment) more addition product is formed. The recovered ketone and phosphonic acid were both very pure as shown by their sharp melting points: this is evidence that no side reactions are appreciable in this length of time. When the components are left in contact for many days, however, other reactions take place; the acid material becomes impure and the non-acid material is no longer unchanged ketone but some oily substance.

**The Addition of Phosphorus Tribromide to Benzal-acetophenone.**—Phosphorus tribromide combines with benzal-acetophenone even more readily than the trichloride. The reaction was investigated by bringing the materials together and after a given time decomposing with water as described in the experiment with the trichloride. In this case, however,  $\beta$ -bromobenzyl-acetophenone was obtained as the non-acid material instead of the unchanged ketone. This was probably due to the addition of hydrobromic acid to the unsaturated ketone during the decomposition of the mixture with water; an oily mass is at first formed which it takes some minutes to decompose completely by agitating with water. When the reaction mixture was poured into dil. sodium hydroxide solution instead of water, most of the non-acid material was unchanged ketone.

The following results were obtained with equimolecular quantities.

Hours.	Acid g.	Ketone equivalent.	Per cent. reacted.
1	3.7	2.6	52
1	3.2	2.2	44
2	3.6	2.5	50
4	3.6	2.5	50

It is evident that the equilibrium is much more in favor of the addition product with phosphorus tribromide than with phosphorus trichloride.

**Reaction in Acetic Acid.**—5 g. of benzal-acetophenone was mixed with 6.8 g. of phosphorus tri-bromide (10% excess) and 7 g. of acetic acid. The ketone dissolved and the reaction mixture then became quite warm while fumes of acetyl bromide were apparent. After standing for 3 hours the mixture was poured into water and the materials were separated in the usual way. 6.2 g. of pure phosphonic acid was obtained (88%) and 0.5 g. of unchanged ketone.

### Summary.

1. The addition reactions of the phosphorus halides with carbonyl compounds are of a different type from the reactions of most reagents with these substances. They involve the formation of a cyclic compound with the increase in valence of a single atom while the more usual reactions take place with the cleavage of the reagent into two parts. The reaction is reversible.

2. This new type of reaction is analogous to addition reactions of inorganic chemistry such as the addition of the halogen acids to ammonia.

3. Lewis' theory of the cubical atom has been applied to this problem. The positive nucleus of the carbon atom of the carbonyl group is exposed by the drawing away of the electrons of the double bond. This exposed nucleus behaves in addition reactions like a positively charged atom and unites with atoms having unshared electrons (the phosphorus atom in the trichloride and the nitrogen atom in ammonia).

4. The resulting addition compounds may undergo various irreversible intramolecular changes or react irreversibly with other reagents. In such cases stable products will be formed.

5. This hypothesis is applied to the 1,2 and 1,4 addition of phosphorus halides, ammonia and its derivatives, the Grignard reagent and phosphorus pentachloride. The reactions of ethylene oxide are also considered.

6. Phosphorus tribromide combines with benzal-acetophenone in the 1,4-position, the reaction being parallel to that with the trichloride. The equilibrium has been measured for both substances; it is more in favor of the addition product in the case of the tribromide than with the trichloride.

[CONTRIBUTION FROM THE MELLON INSTITUTE FOR INDUSTRIAL RESEARCH.]

THE ELIMINATION OF HYDROGEN CHLORIDE FROM CHLORO-HYDROCARBONS.<sup>1</sup>By W. F. FARAGHER<sup>2</sup> AND F. H. GARNER.<sup>3</sup>

Received May 9, 1921.

The preparation of unsaturated compounds from aliphatic chloro compounds by the action of high temperatures was investigated by Nef.<sup>4</sup> His work, which was limited to ethyl, propyl, and *isobutyl* halides showed that ethyl chloride was completely dissociated into ethylene and hydrogen chloride at a temperature of 550°, propyl and *isobutyl* chlorides being completely converted in an analogous manner at 500°. The contact materials used by Nef were pumice stone and soda-lime.

Sabatier and Mailhe<sup>5</sup> in 1904 succeeded in preparing alkylenes from the corresponding aliphatic monochlorides by using as catalysts the chlorides of the divalent metals (Ni, Co, Fe, Cd, Pb, Ba, etc.) at 260°. By this method ethyl, propyl, *isobutyl* and *iso-amyl* chlorides when passed over barium chloride gave the corresponding olefins. At the same time the barium chloride used became gray in color owing to the simultaneous polymerization of a small proportion of the olefins formed. These authors found that the chlorides of monovalent elements exerted no catalytic action even at 350°.

Alumina was found by Senderens<sup>6</sup> to remove hydrogen chloride from propyl and *isobutyl* chlorides at 250°, whereas with no catalyst present *isobutyl* chloride was quite stable at 430°.

At 350°, propyl and *isobutyl* chlorides gave, with alumina as catalyst, yields of 97% of propylene and 95% of *isobutylene* respectively.

The cleavage of hydrogen chloride from mono- and dichloro-cyclohexanes by the use of the catalysts recommended by the above authors has been patented by the Badische Anilin-u. Soda Fabrik in a series of patents: U. S. patent 1,221,382 (1917); Brit. patent 5,429 (1912); and Ger. patents 254,473 and 255,538 (1913). The preparation of isoprene and similar diolefins from chlorinated derivatives of pentane and hexane under reduced pressure using alumina and barium chloride as catalysts has also been patented by this firm (French patents 435,312 and 434,586 (1911), Brit. patents 10,826 and 18,356 (1911) and Ger. patent 255,519).

<sup>1</sup> Copy of address read before the Petroleum Section of the American Chemical Society at Rochester, N. Y., April 27, 1921.

<sup>2</sup> Senior Fellow (Oil Fellowship) Mellon Institute of Industrial Research, of the University of Pittsburgh, Pittsburgh, Pa.

<sup>3</sup> Industrial Fellow (Oil Fellowship) of the Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

<sup>4</sup> Nef, *Ann.*, 318, 1 (1901).

<sup>5</sup> Sabatier and Mailhe, *Compt. rend.*, 138, 407 (1904); 141, 238 (1905).

<sup>6</sup> Senderens, *ibid.*, 146, 1211 (1908), and *Bull. soc. chim.*, [4] 3, 827 (1908).

The present investigation was undertaken with chlorine compounds of hexane, heptane, and cyclohexane in order to determine the most suitable conditions for the preparation of unsaturated compounds therefrom. It was also desired to ascertain the relative stability of dichloro- and monochloro compounds with various catalysts at the high temperatures involved in these dechlorinations. As the cleavage of these chlorides into hydrogen chloride and olefins or diolefins is always accompanied by a complete decomposition of a portion of the hydrocarbons formed, it is obvious that the catalyst must lose some of its effect as the reaction is prolonged owing to the deposition of carbon. This question was investigated by finding the change in catalytic activity as the same catalyst was used continuously for dechlorination.

Hexane, *isohexanes* and heptane fractions were isolated from Pennsylvania straight-run gasoline by repeated fractionations; aromatic hydrocarbons were removed by means of a sulfuric-nitric acid mixture and the fractions redistilled several times through a 120 cm. Hempel column filled with magnesium turnings, and covered with asbestos paper; thus the fractions finally obtained were nearly pure hexane and heptane. Fractions 61° to 64°, 67.5° to 70°, and 97° to 100°, (all at 760 mm.) were collected, representing a mixture of *isohexanes*, *n*-hexane, and *n*-heptane respectively.

Cyclohexane obtained from the Dayton-Wright Division of the General Motors Corporation was carefully freed from benzene and refractionated twice, the fraction of boiling point 79° to 79.5° (740 mm.) being collected; the cyclohexane used for the preparation of chloro compounds melted at 4.5°. The product, therefore, was practically pure cyclohexane.

The paraffin hydrocarbons contained small amounts of polymethylenes as a result of their source and method of preparation. Owing to the comparatively large amounts required for this investigation, however, it was considered that the only practicable method was to isolate from a suitable gasoline all of the paraffin hydrocarbons required.

**Chlorination.**—Cyclohexane was chlorinated in the manner briefly described by Sabatier and Mailhe.<sup>7</sup> By the chlorination of 300 g. of cyclohexane at a temperature of 20° to 25° until an increase in weight of 50 to 75% of that theoretically required for the production of monochloro-cyclohexane was realized, the following products were obtained after several fractionations.

	G.
Cyclohexane recovered unchanged.....	40
Fraction 139–144°, monochloro-cyclohexane ( $d_4^{20}$ 1.002).....	150
Fraction 75–85° (15 mm.), dichloro-cyclohexane ( $d_4^{20}$ 1.179).....	105
Fraction 95–105° (15 mm.), trichloro-cyclohexane ( $d_4^{20}$ 1.266).....	24
Intermediate fractions and residue.....	50

<sup>7</sup> Sabatier and Mailhe, *Compt. rend.*, 137, 240 (1903).

The dichloro- and trichloro-cyclohexanes were purified by two distillations at a pressure of 15 mm.

Hexane and *isohexane* were chlorinated in the vapor phase as first suggested by Schorlemmer<sup>8</sup> and also employed by Michael and Turner.<sup>9</sup> In our procedure, chlorine was introduced at about the middle point of a tube through which the hydrocarbon was being refluxed. A thermometer was inserted at the position where the chlorine was introduced and by this arrangement the course of the chlorination was followed closely.

By this method monochloro derivatives were the principal products and very small amounts of dichloro and more highly chlorinated compounds were formed. It was, however, essential that this chlorination be carried out in diffused light, as in full daylight a flame appears and carbon is formed. In order to obtain quantitative yields it is necessary to resort to absorption or very efficient cooling of the issuing hydrogen chloride, as otherwise some of the chlorinated products will be carried away with it and thus be lost.

The chlorinated products were washed with dil. alkali and water to free them from hydrochloric acid. With some of the chlorinated compounds it was necessary to use brine instead of water owing to the fact that the specific gravities of the compounds were very close to that of water.

A fraction distilling from 120° to 124° which was obtained from the chlorinated *n*-hexane after 4 fractionations, corresponds to 2-chloro-*n*-hexane.

Similarly, from the *isohexane* a fraction distilling from 119° to 123° was isolated. This fraction was a mixture of monochloro-hexanes.

Heptane was chlorinated in a way similar to that used with cyclohexane as already described.

Dichloro-heptanes constituting the fractions boiling from 90 to 100° (15 mm.) and monochloro-heptane forming the fraction 150 to 160° (760 mm.) were obtained after three fractionations.

The specific gravities and iodine numbers of these chloro compounds were determined. The iodine numbers of the chloro compounds were in all cases very small and in all probability were due to the presence of small amounts of olefins.

**Dechlorination.**—In the dechlorination process the chloro compounds were passed at the desired temperature through a glass tube which contained the catalyst. The products of the reaction were then led through a tube containing soda-lime maintained at a temperature of 100° or of 150° and were passed finally into a receiver cooled by an ice-bath. The purpose of the heated soda-lime tube was to remove hydrogen chloride and

<sup>8</sup> Schorlemmer, *Phil. Trans.*, 163, 111 (1872).

<sup>9</sup> Michael and Turner, *Ber.*, 39, 2154 (1906).

thus to prevent its recombination with the olefin. (This reaction was shown by Nef<sup>4</sup> to occur with butylene.) By this means the product obtained by condensation really indicates the true effect of the catalyst. The chloro compound was contained in a buret connected to the tube containing the catalyst through a 2-way glass stopcock; a stream of dry nitrogen could thus be passed through the catalyst when desired. The tube containing the catalyst was heated at 150 to 500° as desired by means of an electric resistance-furnace, the temperature being controlled by a rheostat. The length of the catalyst tube was 70 cm. The soda-lime tube, also, was heated in a similar manner. The temperatures of both the catalyst tube and the soda-lime tube were measured by means of iron-constantan thermocouples. Condensation of the vapors was effected by a tube, surrounded by an ice-bath, which extended into a test-tube with side arm. The side arm was connected to a train of bromine absorption tubes cooled in ice and the latter to a gasometer when desired. The temperature of the soda-lime tube was kept sufficiently high to prevent any of the chloro compound from condensing in this tube, but not high enough for its catalytic effect in the reaction to be measurable. The rate at which the chloro compound was introduced into the tube containing the catalyst could be regulated, with practice to any desired value. The compound was, in general, immediately vaporised owing to the high temperature of the catalyst. After the desired amount of chloro compound had been passed through the tube, the vapors remaining in the tube were driven out by means of a stream of dry nitrogen introduced through the 2-way stopcock and were condensed in the ice-water condenser.

From the percentage of liquid condensed, the yield of dechlorinated product was calculated; see, for example, Table III. The specific gravity and iodine numbers of this condensate indicate the proportion of unsaturated compounds formed, since the iodine number of the unsaturated compound is known. The iodine number serves as an index to the amount of unsaturation only in the case of olefins; in the case of diolefins the iodine value obtained is far below that corresponding to the true extent of the unsaturation. This point will be covered fully in a later paper. The iodine numbers were determined by Hanus method, giving half-hour contact with the iodine solution in the dark (0.10 g. of olefin to 25 cc. of Hanus solution).<sup>10</sup>

The bromine collected any unsaturated compounds which were not condensed by the ice-bath and from the amount of gas evolved during the

<sup>10</sup> It was thought unnecessary to make chlorine determinations on the condensates since a consideration of the specific gravity, iodine number, and distillation characteristics furnishes a sufficiently accurate index to their composition. Owing to the great differences between the boiling points of the chloro compounds and the olefins obtained from them, an analysis by fractionation shows the extent to which the elimination of hydrogen chloride has been effected.

time the liquid was being introduced into the catalyst tube, the extent of decomposition occurring could be ascertained.

The following contact materials were used as catalysts in the dechlorination process: unglazed porcelain, unglazed porcelain which had been soaked in a strong solution of barium chloride and then dried, and alumina (commercial aluminum hydroxide worked to a plastic mass with water, and then dried at the temperature at which it was used); Pyrex glass was used in some experiments since any effect glass may have in the course of the reaction is due presumably to surface action only.

The experiments carried out with the Pyrex glass should, therefore, indicate only the effect of variation of the temperature on the reaction.

**Dependence of Dechlorination on Rate of Introduction of Chloro Compound.**—Experiments were made with monochloro-*isohexane* to determine the effect of varying the rate at which the chloro compound was passed over the catalyst on the amounts of hydrogen chloride removed. These experiments were carried out at 200°, 300°, and 400°, using unglazed porcelain as the catalyst. The soda-lime tube was maintained at 150° during these experiments.

TABLE I.  
IODINE NUMBERS OF CONDENSATES FROM MONOCHLORO-*ISOHEXANE*.  
Iodine number of *isohexene* = 302 (calc.).

Temperature of catalyst, ° C.	Time, Min.	10 cc. passed over catalyst in			
		15.	30.	60.	120.
200	228	209	243	252	
300	246	216	275	290	
400	253	271	263	292	

In general, the iodine numbers and specific gravities of the condensates were in agreement (see, for example, Table III), *i. e.*, the higher the iodine number the lower is the specific gravity.

From these experiments it will be observed that as the rate of introducing the chloro-*isohexane* is lowered, the dechlorination proceeds more completely, but the effect produced by the difference between the two rates, 10 cc. in 15 minutes and 10 cc. in 2 hours, is not very great, inasmuch as fairly complete dechlorination is effected even at 200° by passing 10 cc. over the catalyst in 15 minutes.

It will also be noticed that the effect of temperature from 200° to 400° is not very marked in the preparation of *isohexylene* from chloro-*isohexane*.

As a result of the experiments described in Table I, it was decided to adopt the uniform rate of 20 cc. in one hour for passing the chloro compound over the catalyst in all the experiments described later.

**Loss of Catalytic Power on Prolonged Use.**—These experiments were carried out to determine the effect on the catalytic activity of unglazed

Thus again unglazed porcelain alone acted as a more efficient catalyst than unglazed porcelain impregnated with barium chloride. It will be noted that the dechlorination did not proceed as readily in this case and that apparently a higher temperature is necessary with the dichloro compound than with the monochloro compound. Decomposition of the hydrocarbons also occurred to a greater extent than was the case with the monosubstituted chloro compounds.

TABLE VI.  
CHLORO-HEPTANE;  $d_{40}^{20}$  0.914.  
Iodine Number of Heptylene = 260. (Calc.).  
Iodine Number of Condensates Using Various Catalysts.

Temperature of catalyst. ° C.	Unglazed Porcelain.	Alumina.	Unglazed porcelain barium chloride.	Pyrex glass.
150	100	...	...	...
200	127	198	178	52.5
250	192	238	187	64
300	260	254	170	83
400	265	250	180	181

Alumina is the most active catalyst up to 250° but of all the catalysts used it apparently lost its catalytic effect most rapidly as the result of carbonization. Pyrex glass is inferior to all of the other contact materials in promoting dechlorination at these temperatures and probably brings out only the influence of temperature on the reaction.

From the condensates obtained in these experiments, the olefins were readily separated by fractionation.

Thus, from 70 cc. of chloroheptane condensate the fractions described in Table VII were obtained. It will be noted that Fraction 90 to 110° has an iodine number close to that of heptylene.

TABLE VII.			
Boiling Point. ° C.	Volume. Cc.	$d_{40}^{20}$ .	Iodine Number.
90-110	37	0.744	237
110-145	14	0.823	157
145-155	13	0.903	53

TABLE VIII.  
DICHLORO HEPTANE;  $d_{40}^{20}$  1.068.  
Iodine Number of Heptadiene = 518. (calc.).  
Temperature of catalyst. ° C.

Temperature of catalyst. ° C.	Catalyst.	
	Unglazed porcelain.	Alumina.
200	163	181
300	170	173
350	194	126
400	216	114

Here again it will be noted that alumina is more effective at low temperatures than unglazed porcelain but that its catalytic activity *decreases*



with rise in temperature. A number of experiments carried out with chloro derivatives of cyclohexane, proved that these compounds split off hydrogen chloride more readily than the corresponding aliphatic compounds.

TABLE IX.

Monochloro-cyclohexane; $d_0^{20}$ , 1.003. Iodine Number of Cyclohexene = 310 (calc.).			
Temperature of catalyst. °C.	Unglazed porcelain.	Catalyst alumina.	Pyrex glass.
200	245	260	192
250	275	256	172
300	272	234	214
400	297	152	274

Alumina is the most active catalyst with monochloro-cyclohexane at the lower temperatures; Pyrex glass probably demonstrates again only the influence of temperature in increasing the unsaturation of the product as 400° is approached.

TABLE X.

Dichloro-cyclohexane; $d_0^{20}$ , 1.179. Iodine Number of Dihydro-benzene = 317. (calc.).		
Temperature of catalyst. °C.	Unglazed porcelain.	Alumina.
200	113	132
250	146	167
300	175	170
400	188	117

TABLE XI.

Trichloro-cyclohexane;  $d_0^{20}$ , 1.266.  
Catalyst: Unglazed Porcelain.

Temperature of catalyst. °C.	Specific Gravity.	Benzene. %.
250	1.009	10
350	1.061	..
450	0.984	20

The percentage of benzene was determined by conversion into *m*-dinitrobenzene.

Experiments were also carried out with chlorobenzene, but apparently no dechlorination was produced even at 500°. According to Kramers<sup>11</sup> chlorobenzene is changed slowly into diphenyl and decomposition products at a red heat.

Thus it will be seen that, of the compounds tested, chlorobenzene is the most difficult to decompose and chloro-cyclohexane the most unstable at high temperatures. The condensates obtained from the experiments described above readily gave fairly pure olefins and diolefins on fractiona-

<sup>11</sup> Kramers, *Ann.*, 189, 135 (1877).

tion and this method of removing hydrogen chloride from a chloro compound of a hydrocarbon can be recommended as a general method for the preparation of olefins in the case of monochloro-compounds. In the case of dichloro compounds, the yields of diolefins are small at low temperatures because of poor conversion, while at higher temperatures decomposition of the diolefin produced presumably occurs and there is a poor yield in these cases also.

In the following table are given the properties of some olefins prepared by this method.

TABLE XII.  
Properties of Hydrocarbons.

	Boiling point. °C.	$d_4^{20}$ .	Iodine number.
<i>Isorexene</i> .....	64-65	0.684	294
<i>n</i> -Hexene.....	65-66	0.691	285
<i>n</i> -Heptene.....	97-98	0.727	237
Cyclohexene.....	80-81	0.809	303.5

It is quite unnecessary and useless to prepare a special catalyst for this operation (unless carbonization is prevented by some special method) since the catalyst loses its specific activity after a very short period of service.

### Summary.

1. The chloro compounds of hydrocarbons containing 6 or 7 carbon atoms can be classified in the following order according to the ease with which hydrogen chloride is split off: hydro-aromatic, aliphatic and aromatic.

2. The stability of monochloro compounds of aliphatic hydrocarbons at a given temperature decreases with increasing molecular weight (at least until there are 7 carbon atoms in the chain).

3. There is much more extensive decomposition and greater difficulty in separating all the chlorine from dichloro compounds than from monochloro compounds.

4. Of the three catalysts alumina, unglazed porcelain and unglazed porcelain impregnated with barium chloride, alumina is the most efficient; but all three lose their activity rapidly owing to the "poisoning" produced by the decomposition of the hydrocarbons. (The "poisoning" in these cases is probably a mechanical effect due to the deposition of "carbon" on the catalyst).

5. A method for the preparation of olefins and diolefins from chloro compounds of hydrocarbons has been investigated and the method shown to be quite satisfactory for olefins. With diolefins, secondary decompositions occur and poor yields are obtained.

[CONTRIBUTION FROM THE PHYTOCHEMICAL LABORATORY OF THE BUREAU OF CHEMISTRY  
U. S. DEPARTMENT OF AGRICULTURE.]

## THE ODOROUS CONSTITUENTS OF PEACHES.

BY FREDERICK B. POWER AND VICTOR K. CHESNUT.

Received May 11, 1921.

No information appears to have been recorded hitherto in chemical literature respecting the nature of the substances to which the odor of the peach is due. Although many preparations designated as "Peach Oil" or "Peach Essence" have long been in use for flavoring purposes, it is well known that they consist for the most part of purely empirical mixtures of esters and essential oils with other more specific aromatic substances. The general character of such mixtures also indicates that their components are not such as have actually been found to occur in the fruit whose flavor they are supposed to represent. Inasmuch as the kernels of the peach are sometimes used to impart their particular flavor, which is the same as that of the bitter almond or benzaldehyde, it not infrequently happens that the last mentioned substance is regarded as one of the proper constituents of the peach aroma, but the present investigation has shown that it is not contained in the pulp of the fruit.

### Experimental.

It may be stated in the beginning that throughout this investigation only the fresh pulp of the peach was employed, the pits having been carefully removed. This precaution was naturally of importance in order that the distillate should contain only those odorous substances present in the edible part of the fruit, and to exclude any benzaldehyde which might be produced solely from the pits, especially if broken.

**Special Test for Hydrogen Cyanide.**—It has been stated by Windisch<sup>1</sup> that "all kinds of stone fruits contain in the pulp the elements of hydrocyanic acid. The fruit juices, wines and brandies prepared therefrom, therefore also contain hydrocyanic acid, even when made from the pulp of the fruit with the exclusion of the pits, although in extremely small amount. If the pits are also employed the amount of hydrocyanic acid is considerably increased." In connection with these general observations, reference was particularly made to cherries and plums, although peaches also must naturally be included among the stone-fruits.

A quantity of ripe, free-stone peaches was carefully deprived of the pits, and the pulp, amounting to 5.53 kg., immediately brought into a flask and subjected to distillation in a current of steam. The first small portions of distillate were separately collected. These liquids were perfectly neutral and gave no reaction for hydrogen cyanide by the usual tests. They possessed the characteristic, peach-like odor, but not that

<sup>1</sup> Windisch, *Z. Nahr. Genussm.*, **4**, 819 (1901).

of benzaldehyde, which would doubtless also have been present if hydrogen cyanide were produced from this fruit. The absence of the latter compound was furthermore confirmed by an examination of the first portions of distillate from a very large quantity of peach pulp.

For a complete investigation of the odorous constituents of the fruit, distillations were conducted with separate large portions. The peaches were ripe, in the freshest possible condition, and consisted entirely of the choice variety known as the "Georgia Belle."

### First Distillation.

In order to obtain some information respecting the general characters of the total odorous constituents, a quantity (106.6 kg.) of the fresh peach pulp was distilled in one operation, and without any added water, in a current of steam. The amount of distillate collected was about 65 liters. This liquid was repeatedly cohobated in a current of steam until the odorous substances were finally concentrated in a volume of 4 liters. The large quantity of practically odorless aqueous liquid remaining from this treatment was made alkaline with sodium hydroxide and evaporated, in order to obtain the volatile acids, as will subsequently be described.

The concentrated distillate was practically neutral to litmus, had an exceedingly fragrant odor, and showed a slight oily film on the surface. A small portion of the liquid gave an almost immediate red coloration with sensitized Schiff's reagent, and reduced an ammoniacal solution of silver oxide, soon forming a bright, metallic mirror. With dimethylamine and sodium nitroprusside it gave the beautiful indigo-blue color which is characteristic of acetaldehyde.<sup>2</sup> A special test for formaldehyde by means of phenylhydrazine hydrochloride gave a negative result. No coloration was produced by ferric chloride, which indicated the absence of phenolic substances.<sup>3</sup>

**Test for Methyl Anthranilate.**—Although there was no evidence of the presence of methyl anthranilate, either by the odor or a fluorescence, the concentrated distillate was also examined for this compound. This was done by diluting 5 cc. of the liquid with water, and extracting three times successively with chloroform in portions of 10 cc. each. The chloroform liquids were passed through a dry filter, evaporated on a water-bath in a current of air, and the residue dissolved in 2 cc. of 10% sulfuric acid, this liquid being then treated with sodium nitrite and tested with

<sup>2</sup> THIS JOURNAL, 42, 1511 (1920).

<sup>3</sup> Traphagen and Burke, *ibid.*, 25, 242 (1903), state that they found very small amounts of salicylic acid in a great variety of fruits and vegetables, including apples and peaches. We are unable to confirm their observations with respect to either of the last mentioned fruits.

$\beta$ -naphthol in the manner which has previously been fully described.<sup>4</sup> A completely negative result was obtained.

### Extraction and Characteristics of the Essential Oil.

The entire amount of concentrated aqueous distillate was subsequently extracted five times successively with pure, aldehyde-free ether, the united ethereal liquids were dried with anhydrous sodium sulfate, and the greater part of the solvent was removed by distillation. The residual liquid was then divided into two exactly equal portions, one of which was reserved, while the other was brought into a small tared flask, and the ether allowed to evaporate spontaneously. A small amount of a pale yellow, limpid oil was thus obtained, which possessed an exceedingly fragrant and intense peach-like odor. When cooled somewhat below the ordinary temperature, it formed a concrete, transparent mass, which was interspersed with small acicular crystals, the latter evidently consisting of a paraffin hydrocarbon, as will subsequently be shown. The amount of essential oil thus obtained was 0.3940 g., and as this represented one-half of the original ethereal solution, the total yield of oil was 0.7880 g., or 0.00074 % of the peach pulp employed. In another operation in which 155.6 kg. of pulp of "Georgia Belle" peaches was distilled, and the entire distillate extracted with ether, 1.2774 g. of essential oil was obtained, corresponding to a yield of 0.00082 %.

A trace of the oil, when shaken with a little water, gave all the previously mentioned reactions for an aldehyde, including that characteristic of acetaldehyde. With aniline and a drop of dil. hydrochloric acid it gave the intense red color characteristic of furfural, this compound having doubtless been produced during distillation by the action of the organic acids on the sugar of the fruit. A little of the oil was dissolved in glacial acetic acid and a drop of conc. sulfuric acid added, when a purplish-red color soon developed, similar to that produced by cadinene.<sup>5</sup>

The essential oil from peaches is an exceedingly unstable product. When kept for a few weeks in a narrow glass tube with a capillary constriction, and only occasionally exposed to the air, it became converted into a black, viscid mass, and had then completely lost its original fragrance. It is therefore necessary for its preservation to bring it immediately after extraction from the distillate into a glass tube, which should be hermetically sealed, and when thus protected it appears to remain unchanged.

Inasmuch as one of the above-mentioned color reactions of the oil had indicated the presence of cadinene, it was at first thought that its instability was due entirely to this compound, but the subsequent in-

<sup>4</sup> THIS JOURNAL, 43, 380 (1921).

<sup>5</sup> It may be noted that a somewhat concentrated solution of furfural in glacial acetic acid also gives a coloration with sulfuric acid, but with so small an amount of furfural as that employed for the test with peach oil no perceptible color is produced.

vestigation of the odorous constituents has shown that these are also readily decomposed. It was, nevertheless, thought possible that some further evidence of the presence of cadinene might be obtained, and the remaining half of the above-mentioned ethereal solution, containing 0.3940 g. of the oil, was employed for this purpose. The solution was first saturated with dry hydrogen chloride, and after keeping for several days the ether was allowed to evaporate completely. A small amount of a dark colored product was thus obtained, which was treated with a little alcohol, when some crystalline flakes separated. These were collected and dried on a porous tile. After purification, the substance formed pearly laminae, melting at about  $52^{\circ}$ , and evidently consisted of a paraffin hydrocarbon, since conc. nitric and sulfuric acids had no action upon it. The alcoholic filtrate from the original crystalline substance was evaporated, and the residue treated with ethyl acetate. On allowing the latter solution to evaporate spontaneously, a few fine, colorless needles separated, but the amount of this substance was much too small to permit of its identification. Although no direct evidence of the presence of cadinene in the oil could thus be obtained, it is possible that this was due to the exceedingly small amount of material available for the experiment.

The previously mentioned 4 liters of concentrated distillate, which had been extracted with ether for the purpose of obtaining the essential oil, was subsequently made alkaline with sodium hydroxide and evaporated. The liquid was then acidified with sulfuric acid and distilled in a current of steam, about 1 liter of distillate being collected. This liquid was very faintly acid, and, after treatment with baryta for the purpose of obtaining a barium salt, was found to contain formic acid. The latter was removed by means of potassium permanganate, and the presence of a small amount of acetic acid was then determined by the usual tests. The concentrated distillate, after the extraction of the essential oil, therefore appeared to contain only small amounts of formic and acetic acids.

### Second Distillation.

The product of this distillation was specially designated for an examination of the esters contained in the fruit. The amount of peach pulp employed was 108.4 kg., and about 65 liters of distillate was collected.

### Hydrolysis of the Esters. Evidence of the Presence of Linalool.

The entire original distillate was concentrated by repeated cohobation in a current of steam until the odorous constituents were contained in a volume of about 2 liters. The large quantity of practically odorless aqueous liquid remaining from this treatment was made alkaline with sodium hydroxide, evaporated, and then reserved for the examination of the volatile acids. The concentrated distillate was brought into a

flask provided with a reflex condenser, 25 g. of pure sodium hydroxide added, and the whole kept in a state of active ebullition for one hour. It had then acquired a deep yellow color, and separated a small amount of aldehyde resin. After cooling, the liquid was distilled in a current of steam, the receiver being cooled with ice, and about 800 cc. of distillate was collected. The first portions which passed over were milky, and some oily drops soon separated. This entire distillate, which had a delightful fragrance reminding of linalool, was extracted 5 times successively with pure aldehyde-free ether, and the united ethereal liquids dried with anhydrous sodium sulfate. They then gave no reaction for aldehyde with sensitized Schiff's reagent. The alkaline liquid remaining from the operation of hydrolysis was reserved for the examination of the volatile acids, as subsequently described.

The distillate which had been extracted with ether was saturated with sodium chloride in order to examine it for methyl alcohol. After extraction with light petroleum, it was distilled in a current of steam, about 500 cc. of distillate being collected. This was subjected to 7 successive distillations until the more volatile constituents were finally contained in 2 cc. of liquid, the last two distillates being cooled with ice. A very small portion (0.1 cc.) of this liquid, when oxidized with potassium permanganate in strongly acid solution, developed the odor of formaldehyde, and when further treated according to the method of Denigès, as elaborated by von Fellenberg,<sup>6</sup> a decided reaction for this aldehyde was obtained, a deep bluish-violet color with Schiff's reagent being soon produced. This result established the presence of an exceedingly small amount of methyl alcohol, which may have been formed during the original process of distillation by the hydrolysis of a methyl ester of pectin.<sup>7</sup>

The above-mentioned ethereal extract of the distillate obtained after hydrolysis was distilled in order to remove the greater portion of the ether, and the concentrated residual liquid, which had the odor of linalool, brought into a small pressure flask, in which it was allowed to evaporate spontaneously, the last portion of ether being withdrawn by suction. The yellowish, oily residue had a fragrant odor and contained a small amount of solid substance, which probably consisted of a hydrocarbon. The weight of this residue was 0.2620 g., thus representing 0.00024% of the weight of peach pulp employed, or about one-third as much as the yield of essential oil.

Having ascertained by a preliminary experiment that so small a quantity of linalool as 0.1 g. was capable of yielding on oxidation an amount of citral that could readily be recognized by its odor and some special tests,

<sup>6</sup> Denigès, *Compt. rend.*, 150, 529 (1910); and von Fellenberg, *Biochem. Z.*, 85, 45 (1918).

<sup>7</sup> *THIS JOURNAL*, 42, 1517 (1920).

the above-mentioned oily residue was treated as follows. To the product of hydrolysis, contained in a small pressure flask, there was gradually added, while being kept cool, 5 cc. of a chromic acid mixture,<sup>8</sup> when a transient bluish coloration was first produced. The flask was then closed, and heated on a water-bath, with occasional agitation, at a temperature of about 90° for 15 minutes. The mixture was then cooled, diluted with water, and extracted with 3 successive portions of pure, aldehyde-free ether. The united ethereal liquids, after being washed with a little water, were dried with anhydrous sodium sulfate, and then filtered into a small distilling flask, in which the ether was allowed to evaporate spontaneously. Any ether vapor remaining in the flask was removed by aspiration. The residual product, which had the pronounced odor of citral, was a yellowish oil containing a small amount of solid substance, the latter probably consisting of a paraffin hydrocarbon. A small amount of water was added, and the mixture distilled in a current of steam, about 5 cc. of distillate being first separately collected. This was perfectly neutral to test-paper, contained some oily drops, and had a fragrant, lemon-like odor. A small portion of the liquid on the addition of sensitized Schiff's reagent soon developed a purplish color. It rapidly reduced an ammoniacal solution of silver oxide, and on keeping for some time a bright metallic mirror was formed. The oxidation product thus obtained evidently consisted of citral, but the amount was much too small to permit of the preparation of a derivative. As the hydrolytic product from which it was produced had the pronounced, characteristic odor of linalool, it may safely be concluded that this represents the chief alcoholic constituent of the peach distillate, and that it is present in the form of esters.

#### Acids Obtained by the Hydrolysis of the Esters.

The alkaline liquid remaining after the distillation of the linalool from the previously described operation of hydrolysis was united with a similar liquid obtained by the hydrolysis of a distillate from 14.18 kg. of peach pulp, which will subsequently be noted, and the whole filtered in order to separate a small amount of aldehyde resin. The liquid was then acidified with sulfuric acid and distilled in a current of steam, about 1.5 liters of distillate being collected. The first portion of the distillate was strongly acid, cloudy, and separated a slight oily film on the surface. The entire liquid, which had an odor resembling that of the higher fatty acids, was made alkaline with baryta, concentrated, and the excess of baryta removed by carbon dioxide. The filtered liquid rapidly reduced mercuric chloride and silver nitrate, and evidently contained a considerable amount of formic acid. This was removed by treatment with a 4% solution of potassium permanganate, a current of carbon dioxide being meanwhile

<sup>8</sup> *J. prakt. Chem.*, **45**, 599 (1892).



passed through the liquid. The filtered, neutral solution of barium salts then gave with silver nitrate a small amount of a precipitate, which was collected and analyzed.

Fraction I. Subs., 0.0377: Ag, 0.0164. Calc. for Ag,  $C_8H_{15}O_2$ : Ag, 43.0. Found: 43.5.

This result indicated the presence of caprylic acid, of which further conclusive evidence was subsequently obtained.

The filtrate from the preceding salt gave no further precipitate by the direct addition of silver nitrate, but after concentration it yielded the following additional portions of silver salt.

Fraction II. Subs., 0.0188: Ag, 0.0105. Found: 55.8.

Fraction III. Subs., 0.0502: Ag, 0.0306. Found: 60.9.

Although Fraction II agrees well with silver butyrate, which requires Ag = 55.4%, this is regarded merely as a coincidence, since this fraction as well as Fraction III, when moistened with dil. sulfuric acid, developed the unmistakable odor of valeric acid. The two fractions undoubtedly consisted of mixtures of silver valerate and acetate, these salts requiring respectively Ag = 51.7 and Ag = 64.6%. The total amount of silver salt from the acids obtained by hydrolysis was 0.1653 g. On evaporating the final mother-liquor from these salts, and heating the residue with a little alcohol and strong sulfuric acid, the characteristic odor of ethyl acetate was developed. It may thus be considered that by the hydrolysis of the esters, formic, acetic, valeric and caprylic acids are produced.

### Third Distillation.

It was observed in connection with some preliminary tests of the peach distillate that an appreciable amount of acetaldehyde was present. In order to confirm the identity of this substance and also to ascertain whether any other aldehydic, or possibly ketonic, compound was contained in the fruit, the entire product of one distillation was employed chiefly for this purpose. A considerable quantity (120.2 kg.) of peach pulp was accordingly distilled with steam, and about 65 liters of distillate collected. This liquid was concentrated by repeated cohobation in a current of steam until the odorous constituents were eventually contained in a volume of 2 liters. The large quantity of practically odorless liquid remaining from this operation was made alkaline with sodium hydroxide and evaporated, in order to obtain the volatile acids, as in the case of the previous distillations.

### Identification of Acetaldehyde.

The above-mentioned 2 liters of concentrated distillate was saturated with sodium hydrogen sulfite, and this solution was unavoidably kept for a period of 6 weeks before further treatment. It was then extracted

thrice successively with pure aldehyde-free ether in order to remove the uncombined substances, the united ethereal liquids being washed with small portions of water, dried with anhydrous sodium sulfate, and reserved for further examination. After passing a current of air through the acid sulfite solution to remove any dissolved ether, sufficient sodium carbonate was added to render it distinctly alkaline, and the mixture distilled in steam, about one liter of total distillate being collected. The first portion of the distillate was opalescent, and separated a slight oily film on the surface. It possessed a pleasant odor, resembling that of the higher aliphatic aldehydes, and it also gave all of the previously described reactions of this class of compounds, including that characteristic of acetaldehyde.

The above mentioned distillate containing the aldehyde was treated with an alkaline solution of potassium permanganate until after keeping for some time the red color remained permanent. After separating the manganese dioxide, the excess of permanganate was removed by the addition of a solution of ferrous sulfate in dil. sulfuric acid, and the acid liquid distilled in a current of steam. About 3 liters of distillate was collected, the first portions of which had a strongly acid reaction and showed a distinct opalescence, but the entire distillate was practically odorless. The acid was converted into a barium salt, from which several fractions of silver salt were obtained and analyzed.

Fraction.	Subs. G.	Ag. found. G.	%.
I	0.0302	0.0189	62.6
II	0.0659	0.0423	64.2
III	0.0396	0.0254	64.2
IV	0.0255	0.0164	64.3
V	0.2158	0.1388	64.3
VI	0.0863	0.0555	64.3
VII	0.0870	0.0559	64.3

Calc. for  $\text{AgC}_2\text{H}_3\text{O}_2$  : Ag, 64.6.

It is evident from these results that the aldehydic constituent of peaches consists almost entirely of acetaldehyde, with a very small amount of a higher homolog.

The total amount of silver salt obtained in the above operation was 0.8330 g., which would correspond to 0.2189 g. of acetaldehyde, or 0.00018% of the weight of pulp employed. Inasmuch as the yield of essential oil, which would contain but little of the aldehyde, was 0.00074%, the proportion of the latter compound in the peach distillate was relatively large. It is a rather remarkable coincidence that the proportion of aldehyde to essential oil is practically the same in peach pulp as that found in the rind or parings of the apple, being in the former about 1:4.1 and in the

latter 1:4.3, but the percentage amounts of both constituents are very much larger in the apple parings.<sup>9</sup>

**Hydrolysis of the Essential Oil Extracted from the Acid Sodium Sulfite Solution.**—As the previously mentioned ethereal extract of the acid sulfite solution might be considered to contain the constituents of the essential oil, with the exception of the aldehyde, it was carefully examined. The greater part of the ether was first removed by distillation, and the residual liquid brought into a small flask in which the ether was allowed to evaporate completely. There then remained a few drops of a yellowish oil, together with some crystalline substance, which probably consisted of a paraffin hydrocarbon. To this oily material a solution of 5 g. of pure sodium hydroxide in 100 cc. of water was added, and the whole heated under a reflux condenser for one hour, after which it was distilled in steam. The distillate, which had a pleasant, but somewhat terpene-like odor, separated a few oily drops. It was extracted thrice with pure, aldehyde-free ether, the ethereal liquid dried with anhydrous sodium sulfate and, after removing the greater part of the solvent by distillation, the last portion was allowed to evaporate in a small pressure flask. To the very slight residue thus obtained, there was added a small quantity of a chromic acid mixture,<sup>8</sup> and the whole heated on a water-bath at a temperature of about 90° for 15 minutes. After cooling, water was added, and the liquid extracted thrice with aldehyde-free ether, the ethereal liquids being then washed with a little water, dried with anhydrous sodium sulfate, and allowed to evaporate in a flask adapted for steam distillation. The scarcely perceptible residue, when mixed with water and distilled, yielded a perfectly neutral distillate, which possessed no odor, and even the first small portion of distillate, which had been cooled with ice, gave no reaction with Schiff's reagent.

Having previously ascertained that the odorous constituents of the peach consist chiefly of the esters of linalool, which must therefore be contained in the essential oil, and it being known that linalool on gentle oxidation with chromic acid yields citral, it can only be concluded that by the above-described treatment with acid sodium sulfite the linalool had become completely decomposed. In order to confirm this supposition 5 g. of linalool was added to 100 cc. of a saturated solution of acid sodium sulfite and the mixture allowed to stand, with occasional agitation, for 5 weeks. It was then extracted with ether, the ethereal liquid washed with water, dried with anhydrous sodium sulfate, and the solvent removed. The

<sup>9</sup> Müller and Osterwelder, *Landw. Jahrb. Schweiz.*, 29, 400, 509 (1915), have noted the occurrence of acetaldehyde in the juice of pears, especially that from over-ripe or soft fruit, and state that it is seldom produced in the apple, which is not in accordance with our observations. Compare THIS JOURNAL, 42, 1522 (1920). The same authors remark that this compound is not present at all, or at most in minute amounts, in sound grapes and, furthermore, that it does not occur in fruits until they are completely ripe.

small amount of substance thus obtained distilled almost completely between 160 and 170° as a colorless liquid which had the odor of terpenes and of which it appeared to consist. On keeping for some time it formed a transparent, jelly-like mass.

**Acids Obtained by the Hydrolysis of the Essential Oil.**—The alkaline liquid remaining from the hydrolysis of the product extracted from the acid sulfite solution, as above described, was acidified with sulfuric acid and distilled in steam. The distillate, which was somewhat opalescent, had a distinctly acid reaction, and an odor reminding of valeric acid. It was made alkaline with baryta, concentrated, and the excess of baryta removed by carbon dioxide. The filtered, neutral solution of barium salt was found to contain some formic acid, and this was therefore removed by treatment with potassium permanganate, the liquid being then filtered and concentrated. On the subsequent addition of silver nitrate a small amount of a purely white silver salt was precipitated, which on analysis gave the following result.

Subs. 0.0211: Ag, 0.0089. Calc. for  $\text{AgC}_8\text{H}_{15}\text{O}_2$ : Ag, 43.0. Found: 42.2.

This result indicated the presence of caprylic acid, and the salt developed a fatty odor on ignition.

As the filtrate from the above-mentioned salt gave no further precipitate on the addition of silver nitrate, it was concentrated, when an additional small amount of silver salt was obtained. This was collected and analyzed.

Subs. 0.0249 : Ag, 0.0148. Found: Ag, 59.4.

The composition and characters of this fraction of salt indicated that it consisted of a mixture of silver valerate and acetate in nearly equal proportions. It may thus be concluded that by the hydrolysis of the small portion of original oily material formic, acetic, valeric, and caprylic acids were produced.

#### Emanation of Acetaldehyde from Ripe Peaches.

Having ascertained, as already noted, that the distillate from peaches contained an appreciable amount of acetaldehyde, it was deemed of interest to determine whether, as in the case of apples,<sup>10</sup> this substance could be detected in the exhalations from the fruit. This operation was conducted by aspirating dry air through a large glass percolator containing a quantity of sound, free-stone peaches. As it was desirable that the fruit should not become over-ripe on keeping, it was in the beginning somewhat hard, and was carefully packed in sections, in order to avoid injury by pressure. The percolator was provided at the bottom with an exit tube which was first connected with a bulb apparatus containing a saturated solution of sodium hydrogen sulfite. To this apparatus a empty gas-washing bottle was attached, and to the latter a similar bottle

<sup>10</sup> THIS JOURNAL, 42, 1523 (1920).

containing some of the acid sulfite solution, the whole being connected through an intervening empty flask with a filter pump, by means of which the air was drawn continuously for 3 days through the entire system. The number of peaches used for this experiment was 260, and their total weight was 15.66 kg. During the operation the peaches had become artificially ripened, and the absorbing apparatus was then detached. The acid sulfite solution, which amounted altogether to 300 cc., was found to possess no fruity odor, as was the case in the previously noted experiment with apples.<sup>10</sup> The liquid was made alkaline with sodium carbonate and distilled, 50 cc. of distillate being first collected, and this was then concentrated by re-distillation to a volume of 5 cc., the receiver having been cooled with ice. A small portion of this liquid, when tested with sensitized Schiff's reagent, gave an almost immediate pink coloration, and with an ammoniacal solution of silver oxide a reduction of the silver soon ensued. It could thus be concluded that a very small amount of acetaldehyde was contained in the emanation of the peach, although not sufficient to afford the specific reaction with dimethylamine and sodium nitroprusside. Since the texture of the outer surface of this fruit is very different from that of the apple, it was naturally to be expected that the exhalation of aldehyde would be relatively small.

**Distillation of the Peach Pulp and Identification of Methyl Alcohol.**—The fruit which had been used for the above-described experiment was carefully deprived of the pits, and the pulp then amounted to 14.18 kg. This was distilled in a current of steam, and about 12 liters of distillate collected. The first portion of the distillate was specially tested for hydrogen cyanide, but with a wholly negative result. The entire distillate was then repeatedly cohobated in a current of steam until the odorous constituents were finally contained in a volume of 0.5 liter, the remaining aqueous liquids, which were practically odorless, being then made alkaline with sodium hydroxide and added to the similar liquids from previous operations for the recovery of volatile acids.

To the above-mentioned concentrated liquid 10 g. of sodium hydroxide was added, and the mixture, contained in a flask provided with a reflux condenser, was kept in a state of active ebullition for one hour. It had then acquired a deep yellow color, due to the presence of aldehyde, and was subsequently distilled, about 300 cc. of distillate being collected. The alkaline liquid remaining in the distillation flask was eventually added to the larger quantity of similar product obtained in a previously described operation. After saturating the distillate with sodium chloride, it was extracted thrice successively with light petroleum ether (b. p. 30 to 55°) in order to remove any higher alcohol or other neutral compound, and the petroleum liquids were reserved for further examination. The aqueous salt

solution was then distilled, about 100 cc. of distillate being first collected, and this was then concentrated by further repeated distillations until the more volatile substances were contained in a volume of 2 cc., the receiver in the later distillations having been cooled with ice. A very small portion (0.1 cc.) of the final distillate, when oxidized with potassium permanganate in strongly acid solution, developed a pronounced odor of formaldehyde, and when further tested with Schiff's reagent in the previously described manner, it gave within 15 minutes a deep bluish-violet color. This result established the presence of a small amount of methyl alcohol, and confirmed the previously noted observation respecting its occurrence. On examining the remainder of the concentrated liquid for ethyl alcohol by means of the iodoform test a wholly negative result was obtained.

**Examination of the Petroleum Extract of the Hydrolyzed Product.**—The above-mentioned petroleum extract of the hydrolyzed product was distilled in order to remove the greater part of the solvent, and the residual liquid allowed to evaporate in a small pressure flask, the last traces of petroleum being then removed by aspiration. A minute quantity of a yellowish oil was thus obtained, and to this was added 1 cc. of a chromic acid mixture.<sup>8</sup> After closing the flask, the mixture was heated for 15 minutes on a water-bath, then cooled, diluted with water, and extracted with 3 successive portions of aldehyde-free ether. The ethereal liquids were washed with a little water, dried with anhydrous sodium sulfate, and allowed to evaporate in a small distilling flask, the last portion of ether vapor being withdrawn by suction. The very slight residue had a distinct odor of citral. It was mixed with a small amount of water, and the whole distilled in a current of steam, about 2 cc. of distillate being first collected. This liquid was neutral, gave a faint pinkish coloration with Schiff's reagent, and quickly reduced an ammoniacal solution of silver oxide, thus indicating that a small amount of linalool was contained in the hydrolyzed product.

**Examination of the Aqueous Liquids Remaining from the Cohobation of the Original Peach Distillates. Evidence of the Presence of Formic, Acetic, Valeric and Caprylic Acids.**

The aqueous liquids from which the odorous constituents had been removed as completely as possible by repeated cohobation in a current of steam were all united, made alkaline with sodium hydroxide, and concentrated. The liquid was then filtered, acidified with sulfuric acid, and distilled in steam until the distillate no longer had a distinctly acid reaction. About 2.5 liters of liquid was thus collected. The first portion of the distillate, which was strongly acid, was cloudy and separated some

yellowish oily drops. It had an odor which was not particularly agreeable, resembling that of the higher fatty acids.

As only the first 0.5 liter of distillate contained some oily drops an attempt was made to separate these mechanically, and this was accomplished by means of a small separatory funnel. The acid was then converted into a barium salt, and this was first treated with a few drops of a dilute solution of potassium permanganate in order to remove traces of a reducing substance. After filtering and concentrating the liquid it gave with silver nitrate a small amount of a white, curdy precipitate, which was collected and analyzed.

Subs. 0.0264: Ag, 0.0113. Calc. for  $\text{AgC}_8\text{H}_{15}\text{O}_2$ : Ag, 43.0. Found: 42.8.

The oily drops thus consisted of practically pure caprylic acid.

After the separation of the small amount of oily acid the entire distillate was made alkaline with baryta, concentrated, filtered, and the excess of baryta removed by carbon dioxide. It was then found that the neutral liquid rapidly reduced mercuric chloride and silver nitrate, which indicated the presence of a considerable proportion of formic acid. This was accordingly removed by treatment with a 4% solution of potassium permanganate in a current of carbon dioxide, and the liquid again filtered and concentrated. On the subsequent addition of silver nitrate two successive fractions of silver salt were obtained, which gave the following results on analysis.

Fraction I. Subs. 0.0570: Ag, 0.0247. Fraction II. Subs. 0.0602: Ag, 0.0259. Calc. for  $\text{AgC}_8\text{H}_{15}\text{O}_2$ : Ag, 43.0. Found: I, 43.3; II, 43.0.

These results afforded further confirmation of the presence of caprylic acid.

The filtrate from the preceding fractions yielded a series of silver salts, which were collected and analyzed.

Fraction.	Subs. G.	G.	Ag found. %
III	0.0383	0.0184	48.0
IV	0.0367	0.0196	53.4
V	0.0869	0.0510	58.7
VI	0.0631	0.0372	58.9
VII	0.0427	0.0266	62.3
VIII	0.0520	0.0366	64.6
IX	0.0718	0.0465	64.7
X	0.0384	0.0208	64.6

Calc. for  $\text{AgC}_8\text{H}_9\text{O}_2$ : Ag, 51.7. Calc. for  $\text{AgC}_2\text{H}_3\text{O}_2$ : Ag, 64.6.

In considering the composition of the above-mentioned series of salts, it may be noted that when very small amounts of most of them were moistened with dil. sulfuric acid they developed the strong and unmistakable odor of valeric acid. It may therefore be concluded that Fraction III consisted of a mixture of silver valerate and caprylate in about equal proportions, and the Fractions IV to VII inclusive, mixtures of silver

valerate and acetate, while the subsequent fractions, as is evident from the figures, represented practically pure silver acetate. The aqueous liquid obtained by the repeated cohobation of the original peach distillate must therefore have contained formic, acetic, valeric and caprylic acids. The total amount of silver salt obtained from the aqueous liquid, of which the fractions analyzed formed a part, was 1.5402 g

### Summary.

The results of the present investigation, for which only the pulp of choice, ripe peaches was employed, may be summarized as follows.

1. The odorous constituents of the fruit may be considered to consist chiefly of the linalyl esters of formic, acetic, valeric, and caprylic acids, together with a considerable proportion of acetaldehyde and a very small amount of an aldehyde of higher molecular weight. It is probable that the volatile acids are present to some extent in a free state.

2. A minute amount of acetaldehyde is contained in the emanation from the entire ripe fruit.

3. No trace of hydrocyanic acid or benzaldehyde could be detected in the distillate from peach pulp. It may therefore be concluded that the occurrence of the glucoside amygdalin is restricted to the kernels of the fruit, and that no compound capable of yielding hydrocyanic acid is present in the pulp.

4. By extracting a concentrated distillate of the peach with ether a very small quantity of an essential oil was obtained. This was a pale yellow, limpid liquid, which possessed an exceedingly fragrant and intense peach-like odor. When cooled somewhat below the ordinary temperature, it formed a concrete, transparent mass, which was interspersed with minute, acicular crystals. These crystals evidently consisted of a paraffin hydrocarbon, which, when indirectly isolated, were found to melt at about 52°. The yield of essential oil was 0.00074% of the weight of pulp employed.

In addition to the above-mentioned esters, the peach oil was found to contain a little acetaldehyde and furfural, the latter having doubtless been produced during the process of distillation by the action of the organic acids on the sugar contained in the fruit. The presence of cadinene, or a compound giving a similar color reaction, was also indicated.

The essential oil of peach is an exceedingly unstable product. When kept for a comparatively short time in a glass tube with a capillary constriction, and only occasionally exposed to the air, it became converted into a black, viscid mass, and had then completely lost its original fragrance. This change is in accordance with the character of the constituents of the oil as determined by the present investigation. If the oil, as first obtained,



be brought into a glass tube, and hermetically sealed, it appears to be capable of preservation for an indefinite period.

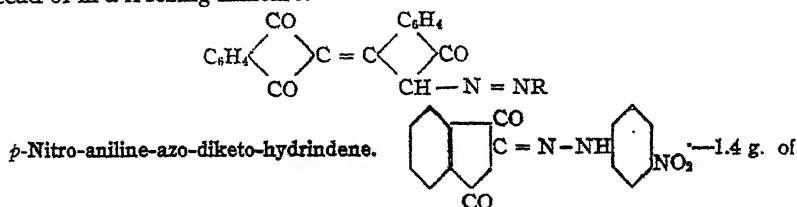
Although a product based upon the results of this investigation may be made synthetically which represents to a considerable degree the fragrance of the peach, the exact reproduction of the natural aroma of the fruit presents an apparently insurmountable difficulty. This is largely due to the fact that in the preparation of its esters linalool undergoes intramolecular changes with the formation of the isomeric compounds geraniol and terpineol or their respective esters, and as these esters have similar boiling points no means are available for their separation. It is also well known that in the esterification of linalool dehydration of the alcohol occurs to some extent, with the formation of terpenes, which are difficult to eliminate completely from the product. This is particularly the case in the preparation of linalyl formate, even when the usual precautions are observed and the ester is distilled in a vacuum. Furthermore, the linalyl esters, when obtained in the purest possible state, are subject to somewhat rapid decomposition on exposure to the air.

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### NOTES.

**Azo Compounds from Diketo-hydrindene.**<sup>1</sup>—It is generally known that substances containing a hydrogen atom replaceable by a metal when treated with diazo chlorides give the corresponding azo compounds. This fact suggested to us that 1,3-diketo-hydrindene which has a  $>\text{CH}_2$  group situated between two "CO" groups would react with diazo chlorides in a similar way, giving azo compounds. We prepared a few azo compounds with *p*-nitro-aniline, benzidine, *p*-toluidine and  $\beta$ -naphthylamine, and diketohydrindene, in the hope that they might be found to be useful as dye stuffs. They all give very insoluble sodium salts, and the colors are very fast. We dyed several pieces of linen with them indirectly; but whether they will be of any commercial interest remains to be seen.

Diketo-hydrindene changes very readily to anhydro-*bis*-diketo-hydrindene. In the case of benzidine we have actually isolated a condensation product of *bis*-diketo-hydrindene and the corresponding diazo compound by bringing about the coupling of the constituents at ordinary temperature instead of in a freezing mixture.



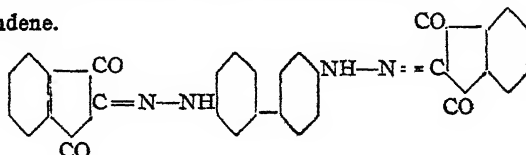
<sup>1</sup> Read before the All-India Science Congress, 1920.

*p*-nitro-aniline was diazotized with suitable precautions and 1.5 g. of diketo-hydrindene dissolved in excess of sodium hydroxide solution was gradually added to it. The temperature was not allowed to rise above 5°. A solid of yellow color separated. This was allowed to stand for 2 hours, was acidified with dil. sulfuric acid, filtered and then thoroughly washed free from acid. This was dried and recrystallized from pyridine. The compound does not melt even at 280°. It dissolves in conc. sulfuric acid with a red color. In potassium hydroxide it dissolves to form a magenta colored solution.

*Analyses.* Subs., 0.1347: CO<sub>2</sub>, 0.3010; H<sub>2</sub>O, 0.0401. Subs., 0.1718: N<sub>2</sub>, 21.6 cc. (24°, 754 mm.).

Calc. for C<sub>15</sub>H<sub>9</sub>O<sub>4</sub>N<sub>3</sub>: C, 61.0; H, 3.0; N, 14.2. Found: C, 60.9; H, 3.2; N, 13.9.

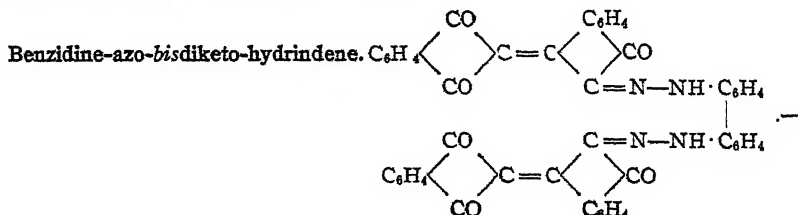
**Benzidine-azo-diketo-hydrindene.**



1.84 g. of benzidine was tetrazotized and to this 3 g. of diketo-hydrindene, dissolved in excess of sodium hydroxide solution was gradually added, the temperature being kept below 5°. This was allowed to stand for some time and then acidified. The dark red precipitate that separated was filtered and washed repeatedly. The compound was insoluble in almost all the solvents, such as alcohols, ether, chloroform acetone, xylene and pyridine. With conc. sulfuric acid it gives a violet colored solution.

*Analysis.* Subs., 0.1649: N<sub>2</sub>, 17.5 cc. (32°, 756 mm.).

Calc. for C<sub>30</sub>H<sub>18</sub>O<sub>8</sub>N<sub>4</sub>: N, 11.3. Found: 11.3.

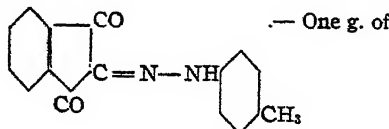


1.84 g. of benzidine was tetrazotized as usual and to this an equivalent quantity of alkaline solution of diketo-hydrindene was added. The solution was kept overnight at ordinary temperature (about 26°), then acidified, filtered and washed.

*Analysis.* Subs., 0.2294: N<sub>2</sub>, 14.9 cc. (28°, 766 mm.).

Calc. for C<sub>48</sub>H<sub>26</sub>O<sub>8</sub>N<sub>4</sub>: N, 7.6. Found: 7.5.

***p*-Toluidine-azo-diketo-hydrindene.**



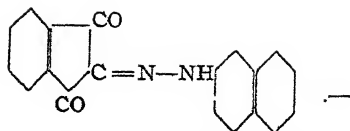
— One g. of

*p*-toluidine was diazotized in the usual way and coupled with 1.5 g. of diketo-hydrindene in sodium hydroxide solution at 5°. This was acidified, filtered, washed and dried. It was recrystallized from acetic acid. It separated in fine yellow silky flakes, melting at 211°. It dissolves in conc. sulfuric acid to form a chocolate colored solution.

*Analysis.* Subs., 0.1743; N<sub>2</sub>, 16 cc. (23°, 756 mm.).

Calc. for C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>: N, 10.6. Found: 10.3.

$\beta$ -naphthylamine-azo-diketo-hydrindine.



1.43 g. of  $\beta$ -naphthylamine was diazotized and coupled with 1.5 g. of diketo-hydrindene in alkali solution at 5°. This was acidified, filtered, washed and dried. It was recrystallized from acetic acid. It melts at 205°. It forms a deep brown colored solution.

*Analysis.* Subs., 0.1439. N<sub>2</sub>, 12 cc. (26°, 754 mm.).

Calc. for C<sub>19</sub>H<sub>15</sub>O<sub>2</sub>N<sub>2</sub>:N, 9.3. Found: 9.17.

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Received April 23, 1921.

**The Odorous Constituents of Apples.**—It has come to our notice that a paper has been published by Shintarô Kodama<sup>1</sup> which, as abstracted in *J. Chem. Soc.*, 120, i, 220 (1921) bears the following title: "Odorous Constituents of Apples. Esters Derived from Leucic Acid." In the original publication the title of the paper is: "On the Odor of Apples. Ethereal Oils Obtained from Leucic Acid." After stating, "Power and Chesnut have proved that amyl esters of formic, acetic, and hexoic acids are the principal odorous constituents of apples,"<sup>2</sup> Kodama proceeds to describe certain esters prepared from by-products of the decomposition of proteins, such as ethyl  $\alpha$ -acetoxy-*iso*-hexoate, and the corresponding methyl ester; ethyl  $\alpha$ -benzoyloxy-*iso*-hexoate; ethyl  $\alpha$ -isovaleryl-*iso*-hexoate, etc. Inasmuch as these compounds or "esters derived from leucic acid" do not occur in apples, and therefore do not represent their odorous constituents, the title given by Kodama to his communication is not only misleading but entirely unwarranted. It has consequently seemed desirable to call attention to these facts in order to avoid any possible confusion in the literature on the subject.

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**The Occurrence of Methyl Anthranilate in Grape Juice.**—The use of fruit juices as beverages has become more extended and greatly increased in recent years, and considerable attention is now being given to the control of their quality and purity. One of the substances that has been suspected of being added to natural grape juice for the purpose of improving its flavor is methyl anthranilate, and it is well known that this compound,

<sup>1</sup> Kodama, *J. Tokyo Chem. Soc.*, 41, 965-975 (1920).

<sup>2</sup> THIS JOURNAL, 42, 1509-26 (1920).

in a dilute state, possesses a decided grape-like odor. Inasmuch as the examination of some samples of commercial grape juice, according to the method recently published by one of us,<sup>1</sup> has clearly indicated the presence of methyl anthranilate, some of those interested in these products appear to have been led to the conclusion that in such instances an artificial flavoring agent had been employed. In consequence of these deductions it has naturally become of much importance to determine whether a pure and entirely unsophisticated grape juice may not contain small amounts of methyl anthranilate. An opportunity for conducting such an investigation has been made available through the kind cooperation of Dr. J. S. Caldwell, of the Bureau of Plant Industry, U. S. Department of Agriculture, who has provided us with a large number of samples of grape juice expressed by himself during the autumn of 1920 from many different and well determined varieties of the fruit. Although the examination of all these samples has not yet been completed, the observations that have thus far been made enable us to conclude that methyl anthranilate is a natural and apparently constant constituent of grape juice. The amounts that are present in the numerous varieties of the grape appear to differ very greatly, and by far the most decisive results of the test have thus far been obtained from the red juices of the Concord type. By the distillation of 500 cc. of the grape juice the amount of methyl anthranilate found has in no case exceeded 0.001 g., as determined by comparative tests with the pure substance, but even this small amount, as has previously been shown,<sup>1</sup> is sufficient to produce a deep red color or precipitate by the interaction of the diazotized compound with  $\beta$ -naphthol. In the case of the light colored juices the amount of methyl anthranilate present, as indicated by the distillation of 500 cc. of liquid, has thus far been observed to be not more than 0.0001 g., and is frequently less, but in few instances could it be regarded as entirely absent.

It has seemed to us desirable to present these preliminary observations regarding the occurrence of methyl anthranilate in grape juice in order that those engaged in the examination or control of commercial products may not be led to wrong conclusions respecting their purity. The more complete results of the investigation of this subject must necessarily be reserved for a later communication.

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<sup>1</sup> THIS JOURNAL, 43, 377 (1921).

## NEW BOOKS.

**James Cutbush: An American Chemist, 1788-1823.** By EDGAR F. SMITH, Provost of the University of Pennsylvania. Printed by J. B. Lippincott Co., Philadelphia, 1919. 94 pp. 10 × 14.5 cm.

As a result of his investigations of chemical development in this country Dr. Smith has given us "Chemistry in America" (1914), "Life of Robert Hare, 1781-1858" (1917), "James Woodhouse, A Pioneer in Chemistry" (1918), "Chemistry in Old Philadelphia" (1918), and now "James Cutbush," through which he has perfected the record of early chemical achievements for his native country, for the State of Pennsylvania in which he was born, for the city of Philadelphia in which he has long resided, for the University he has served so well during upwards of four decades, and for the profession in which he occupies so distinguished a position.

There is a marked contrast in the treatment of Hare in the portly volume of 508 pages, 16 by 23.5 cm. in area, with a colored portrait, and of Cutbush in this modest little pocket edition, and yet the latter appears in some ways the more fascinating, since Dr. Smith has brought to our attention a man of mystery, and also an almost mythical college.

From the record we learn that in 1808, and when but 20 years of age, Cutbush published in the Philadelphia "Medical Museum" a paper on mercury fulminate, giving the results of his endeavor to produce this body by a method in which no alcohol was employed and announcing his discovery of a mercury oxalate that was exploded by percussion. Also he published in that year a book called the "Useful Cabinet" which appears to have been a compilation of useful scientific facts and formulas. Moreover, in the "Aurora," a Philadelphia daily paper, he published in that year fifteen articles dealing with the Application of Chemistry to Arts and Manufacture which covered a wide variety of topics. While writing this review there are before me two maps showing the location in the United States of establishments of certain selected chemical industries in 1900 and in 1915 in each of which it is apparent that these industries center about Philadelphia, and history records our earliest factories in that city. One may well believe that Cutbush's active propaganda continued by public lecture courses, investigations, and publications, throughout his brief life, materially contributed toward this consummation.

In the 15 years following his first appearance in print, besides many journal articles covering his investigations, which appeared in the *American Journal of Science* and other periodicals, Cutbush published in 1812 a book on "Hydrostatics," dealing with hydrometers and their applications, in which there appeared numerous tables as well as many interesting and serviceable problems; in 1813 his "Philosophy of Experimental Chemistry" in two volumes; in 1814 the "American Artists' Manual" in two volumes, of more than 600 pages each, which was a popular dictionary of chemical

technology; in 1821 a "Synopsis of Chemistry" arranged alphabetically, comprehending the names, synonyms and definitions in that science which seems in a manner to have been a forerunner of Couch's admirable "Dictionary of Chemical Terms;" and in 1823 "Lectures on the Adulteration of Food and Culinary Poisons. . . . with a means of discovering them and rules for determining the purity of substances." This book was published at Newburgh, N. Y. and from its title Cutbush appears at that date to have entered the field so actively developed later by Wiley. In 1825, two years after his death, there was published in Philadelphia his "System of Pyrotechny" comprehending the theory and practice, with the application of chemistry, and covering 612 pages, with 44 pages of introduction.

While thus actively engaged in investigation and publication Cutbush carried on the business of "Chemist and Apothecary" at 25 S. Fourth St., Philadelphia, where, by his advertisement in 1819, it appears "complete collections of chemical reagents are kept as usual" and where "bleaching liquor, artificial musk, phosphate of mercury and other chemical preparations are prepared and sold." He gave numerous courses of public lectures and was, at the age of 23, President of the Columbian Chemical Society. He became Vice President of the Linnean Society, a founder of the Society of Philadelphia for the Promotion of National Industry, a member of the American Philosophical Society, and Professor of Chemistry, Mineralogy and Natural Philosophy in St. John's College, Philadelphia, but beyond learning that Benj. Smith Barton was professor of natural history and botany in the college, a Mr. Greiner taught there, and that the Rev. Mr. Bachman was president, Dr. Smith was not able to gather by extended search any further information as to the existence or location of this institution.

In 1814 Cutbush was appointed to the U. S. Army, with the rank of assistant apothecary-general, serving first in Philadelphia and later in the Northern division. From May 1820, he was chief medical officer of the U. S. Military Academy and Post at West Point until, on the reorganization of the Army, he became, on September 1, 1820, Post Surgeon and Acting Professor in the newly created department of Chemistry, Mineralogy and Geology, which he held until his death in 1823. Among his successors in this professorship were Dr. John Torrey, widely known as a botanist, and J. W. Bailey, an authority on the infusoria and they together with Hassler, Ellicott, Weir, and others selected by Col. Sylvanus Thayer, the "Father of the U. S. Military Academy," who were investigators and producers, as well as teachers, gave the prestige to "West Point" as an educational institution it has long continued to enjoy. Of all those who have held the professorship of chemistry, mineralogy and geology at West Point up to the present Cutbush appears to have been the only one who was primarily a chemist, though Torrey held the professor-

ships of chemistry in the College of Physicians and Surgeons, Princeton College and the College of the City of New York, and served as U. S. Assayer at New York from 1853 to 1873.

Dr. Smith designates the "System of Pyrotechny" as "the real *magnum opus* of Cutbush;" it "bears the earmarks of much careful study. It is a most worthy contribution, and is strong proof of the dominating force in the mind of Cutbush, namely, to make his science as widely useful as possible. Chemists may justly take pride in this early contribution in the application of chemical principles." He might have added that the book is "good authority" to-day and that it is doubtful whether any later book on this subject is as valuable a guide to pyrotechny or so filled with erudition.

It is obvious that the development of the rocket as an implement of warfare by Congreve was an impelling motive in the writing of this Pyrotechny for, after successful use in the bombardments of Copenhagen and Boulogne, the siege of Flushing, and the battle of Leipzig, Congreve rockets assumed an importance in the Napoleonic Wars comparable with that of the drop bomb, depth bomb, and poison gases in the Great War. The preparation and publication of this Pyrotechny was opportune and of special value to our military services, and in its preparation Cutbush wisely obeyed the principle that an application in an art is best advanced by a scientific survey of the art as a whole.

Commenting on the Aurora articles published when Cutbush was a "lad of twenty years" Dr. Smith says, "they show a wide, general knowledge and also great familiarity with the science of chemistry." The "System of Pyrotechny" is replete with learning, and besides his knowledge of chemistry and physics it evidences a wide acquaintance with foreign literature, more especially that of France yet after extended search the biographer says "Indeed, it will probably remain a query as to where he was educated."

Provost Smith has produced a delightful little book which cannot fail to entertain and enlighten all who may have the good fortune to read it.

CHARLES E. MUNROE.

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**La Tension de Vapeur des Mélanges de Liquides: L'Azéotropisme.** (The Vapor Pressure of Mixtures of Liquids: Azeotropism). By MAURICE LECAT. Vol. I, Experimental Results and Bibliography. Henri Lamartin, Brussels, 1918. xii + 319 pp., 200 figures. 19 X 25 cm. Price, 45 fr.

This admirable book is the first of a two-volume work devoted to a study of azeotropic liquids, that is, liquid mixtures which exhibit a maximum or a minimum boiling point.

Although the importance of this subject was evident from the researches of Roscoe in 1859-60, there has been surprisingly little advance in our knowledge regarding the prevalence of this phenomenon. In 1899,

Ryland out of 80 mixtures which he examined found no less than 45 instances of azeotropism. This led Lecat to a still wider exploration, with the result that 1050 new azeotropic mixtures were discovered.

In this volume the author first gives an introduction of 60 pages to the general theory of the vapor pressure of liquid mixtures. It is a thorough, competent, and quite the most up-to-date treatment of the subject extant. It is replete with interesting and provocative footnotes, and indicates a wide and careful study of the literature.

The second and principal part of this volume is devoted to tables of data having to do with some 2450 mixtures. In addition to the azeotropic constants, in cases where this phenomenon is shown, there are also given the density and the change of volume and of temperature on mixing. In addition boiling-point curves, total and partial vapor curves, and similar information are given whenever available. So far as possible, these data are arranged chronologically and provided with elaborate cross references to the bibliography. There are also three tables, two for binary systems showing either a maximum or a minimum vapor-pressure curve, and one for ternary systems.

These tables are followed by a list of some 1500 substances distilling at ordinary pressure and grouped under different classes such as alcohols, acids, esters, etc., arranged in order of decreasing volatility. In addition to the boiling point, the melting point, density, and critical constants are given when they are known with sufficient accuracy.

The third and last part of the volume (52 pages) contains a very excellent and valuable bibliography. In it are given first, an alphabetical list of authors with complete titles and references to their publications; second, a list of these publications (760) chronologically arranged; third, a list of the 118 periodicals or journals cited, indicating the volumes and pages where the articles appear. Each list is carefully cross referenced.

Added to the end of the book are some notes on the preparation of certain rather rare substances such as cyclohexene, isoprene, etc., in a high state of purity. There is also a rather irrelevant article by the author on the reaction of phenols, etc., with olefine hydrocarbons.

The author announces a second volume of some 400 pages devoted to a mathematical theoretical treatment of the subject.

This book merely as a compilation of our present information on this subject represents a notable achievement. If the author's experimental work proves to be as excellent as his bibliographic achievements, the completed volume will surely rank as a classic in this special field.

For this reason it is to be regretted that the author has not been able to keep certain personal grudges and animosities out of his footnotes. They certainly tend to undermine the confidence of the reader in the good judgment of the author. Perhaps they should be charitably forgotten



in consideration of the ill health which the author states he suffered, and the difficulty of doing intellectual work when his country (Belgium) was devastated by war which appeared to him as monstrous as it was insane. This situation is reflected in the dedication of the book which reads,

"To all victims of militarism, to all those, no matter to what nation they belong, who with DuBois-Reymond and Ch. Hermite condemn Chauvinism and place the interests of science above those of politics, I dedicate this work."

ARTHUR B. LAMB.

**"Ammonia and the Nitrides."** By DR. EDWARD B. MAXTED. J. and A. Churchill, London. P. Blakiston's Son and Company, Philadelphia, Pa. 114 pages, 16 illustrations, 18.5 × 12.5 cms. Price, \$2.00

This little book is an excellent summary of the information which can be gathered from the periodical literature relative to the so-called Haber Process and the reactions of free nitrogen.

In the first chapter, the author discusses the ammonia equilibrium, its calculation from the heat of formation of ammonia, and from specific-heat data. Experimental verification of this equilibrium is then presented. In the second chapter, the author describes at some length various types of pressure furnaces and the results which have been obtained with a few "classical" catalysts. The discussion of the synthesis of ammonia at very high temperatures and also by the silent discharge will prove of interest to many readers.

By far the most useful information contained in this book is found in the chapters describing the nitrides. A very fine list of references accompanies these chapters. The book closes with a chapter on active nitrogen.

Considering the great interest in nitrogen fixation this book comes at a very opportune time. However, it will disappoint anyone who expects to find in it anything new on the subject of ammonia synthesis. Had he wished, the author doubtless could have given an excellent discussion of ammonia catalysts, for example; but when we consider the jealous manner in which the different nationals have guarded their knowledge of this most important feature of the Haber Process, this omission is no doubt excusable.

ALFRED T. LARSON.

**Die störenden Einflüsse auf das Eintreten und die Eindeutigkeit analytischer Reaktionen.** By DR. W. STADLIN, Chemiker am kantonalen Laboratorium, St. Gallen. Georg Thieme, Leipzig, 1921. 70 pp. 19.5 × 13.5 cm. Price outside of Germany, M. 18.

This little book records very briefly, in catalog form, the cases in which various well-known qualitative reactions for the different inorganic and organic constituents of substance give unreliable results. Two typical

examples may be cited. Under "Aluminum," six tests are mentioned, of which the first reads as follows: "*1. Precipitation of  $Al(OH)_3$ .* Is prevented by alkali tartrates, malates, and citrates, in general by the presence of organic oxyacids and oxycompounds (sugars, starch, etc.)." Under "Benzoic Acid," three tests are given, of which the first reads: "*1. Detection by oxidation to salicylic acid. a. By means of potash.* Unreliable, because in the fusion process there is formed mainly *p*-oxybenzoic acid, which does not give the  $FeCl_3$  reaction; moreover, the small quantities of possible salicylic acid run the risk of being destroyed by the progressing process of oxidation (Stadlin, *Chem., Ztg.*, 1916, 770). *b. By means of  $H_2O_2$ .* the delicacy of the reaction is dependent on the relation of the hydrogen peroxide to the benzoic acid. Neglect of this fact may lead....." To the inorganic constituents are devoted 25 pages, and to organic substances 30 pages. In a 5-page appendix is included a similar treatment of the methods of testing blood and sperma.

A. A. NOYES.

**The Chemistry and Technology of the Diazo Compounds.** By JOHN CANNELL CAIN. Edward Arnold, London, 1920. xii + 199 pp. Price \$4.20.

This is a second edition of the well-known book which was first published in 1908. The treatment of the subject follows the same lines as in the first edition but the work has been brought up to date by the consideration of many recent investigations. A new chapter on the heterocyclic diazo compounds has been added. Altogether the book has been increased by some 30 pages. This revision of a monograph on one of the most important branches of aromatic chemistry will be welcomed by all organic chemists.

JAMES B. CONANT.

**Organic Chemical Reagents II.** By ROGER ADAMS, O. KAMM, C. S. MARVEL. University of Illinois Bulletin, Urbana, Illinois. October 11, 1920. 57 pp. 5 fig. 15 × 23 cm. Price 75 cents.

The undersigned had the opportunity a year ago<sup>1</sup> to call to the attention of his colleagues to the publication of the exceedingly useful pamphlet, "Organic Chemical Reagents," by Adams, Kamm and Marvel. The second pamphlet in the series has now appeared, describing in detail, as before, the directions for some 23 preparations which have been studied in the Chemical Laboratories of the University of Illinois. "It is desired," the authors say, "to make available to all the most satisfactory methods and reliable directions for producing various organic chemical reagents for which there is considerable demand by technical and university laboratories. A special endeavor has been made to choose wherever possible the method which may be adapted to larger scale work. Care has been

<sup>1</sup> THIS JOURNAL, 42, 1074 (1920).

taken to include all the necessary details so that there will be a minimum of difficulty in making the various substances."

The order of treatment is somewhat different from that in the first pamphlet. We have: (1) Procedure, *i. e.*, directions for the preparation of the substance; (2) Notes, giving the explanations of why it is essential to observe the conditions laid down in the directions; (3) Methods of preparation, listing the various methods in the literature, good and bad. The third caption corresponds nearer to what Beilstein calls B. (Bildung), in distinction from his D. (Darstellung). The following preparations are included in the new publication: nitroso- $\beta$ -naphthol, hydrazine sulfate, phenylhydrazine, phenyl-isocyanate, alkyl and related bromides, camphor sulfonic acid, acetonitrile, benzoyl peroxide, benzyl cyanide, phenylacetic acid, ethylphenyl acetate, fumaric and succinic acids, succinic acid, pinacone hydrate, mesitylene, *p*-nitrobenzoic acid, methyl *m*-nitrobenzoate, *m*-nitrobenzoic acid, *n*-butyl cyanide, *n*-valeric acid, ethyl *n*-valerate, *n*-amyl alcohol, and *n*-amyl amine.

Equally explicit directions and as complete a bibliography characterize Part II of the "Organic Chemical Reagents" as were found in Part I. Every user of these books, and the users will be many,<sup>2</sup> will be thankful to the authors for these two essential features.

M. GOMBERG.

**Vitamines: Essential Food Factors.** By BENJAMIN HARROW, PH. D., Associate in Physiological Chemistry, College of Physicians and Surgeons, Columbia University. E. P. Dutton and Company, 681 Fifth Avenue, New York, 1921. x + 219 pp. 8 figures. 12.5  $\times$  19.5 cm. Price \$2.50 net.

With general recognition of the importance of what may be called the Accessory Food Factors and the part which they play in the maintenance of health, this little volume may be regarded as a timely contribution.

The author has endeavored to present the most salient facts together with the best established theories in small compass and in a popular manner. The jocundly conversational style of the opening chapters will probably effect no hindrance to the fulfilment of the purpose of the book, and the later chapters present excellent summaries in a clear and terse manner. The arrangement of the material is excellent, and the description of the feed-  
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All in all, however, the book offers a simple, direct, and accurate presentation of facts and theories which are of interest and of importance to the laity. It should reach a large part of the community who are desirous of being informed but who are without the background to permit or desire extended consideration of the theoretical implications.

The press work of the book is excellent.

ALLAN WINTER ROWE.

# THE JOURNAL

## OF THE

# American Chemical Society

with which has been incorporated the

American Chemical Journal.

(Founded by Ira Remsen)

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### REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS FOR 1921-22.

A few new determinations of atomic weight have appeared since the publication of our last report. They are, briefly, as follows.

**Aluminum.**—Richards and Krepelka,<sup>1</sup> from analyses of aluminum bromide, find Al = 26.963 when Br = 79.916. This value, rounded off to 27.0, should replace the older figure.

**Bismuth.**—Hönigschmid,<sup>2</sup> from a long series of analyses of the chloride, find Bi = 209.013. Classén and Ney,<sup>3</sup> by conversion of bismuth triphenyl,  $\text{Bi}(\text{C}_6\text{H}_5)_3$  into  $\text{Bi}_2\text{O}_3$ , find Bi = 208.9967. The two values, obtained by very different methods, are in good agreement, and the value 209 may safely be adopted.

**Thulium.**—James and Stewart<sup>4</sup> have determined the ratio  $\text{TmCl}_3$  to 3Ag, which gives Tm = 169.9. This value, as obtained by a good method, should replace the figure now in use which was not supported by detailed evidence. It seems to have been only a preliminary determination which does not claim to be final.

**Nickel.**—In 1915 Baxter and Parsons published a preliminary comparison of the atomic weights of terrestrial and meteoric nickel, which

<sup>1</sup> Richards and Krepelka, *THIS JOURNAL*, 42, 2221 (1920).

<sup>2</sup> Hönigschmid, *Z. Elektrochem.*, 26, 403 (1920).

Classén and Ney, *Ber.*, 53, 2267 (1921).

<sup>4</sup> James and Stewart, *THIS JOURNAL*, 42, 2022 (1920).

was noted in the report of the committee shortly afterwards. They have now published their complete paper<sup>5</sup> and give the following values: terrestrial nickel, Ni = 58.702; meteoric nickel, Ni = 58.685. The agreement is very close, and within the range of variation ascribable to experimental errors.

## INTERNATIONAL ATOMIC WEIGHTS, 1921-22.

Symbol.	Atomic weight.	Symbol.	Atomic weight.
Aluminum.....Al	27.0	Molybdenum.....Mo	96.0
Antimony.....Sb	120.2	Neodymium.....Nd	144.3
Argon.....A	39.9	Neon.....Ne	20.2
Arsenic.....As	74.96	Nickel.....Ni	58.68
Barium.....Ba	137.37	Niton (radium emanation)Nt	222.4
Bismuth.....Bi	209.0	Nitrogen.....N	14.008
Boron.....B	10.9	Osmium.....Os	190.9
Bromine.....Br	79.92	Oxygen.....O	16.00
Cadmium.....Cd	112.40	Palladium.....Pd	106.7
Calcium.....Ca	40.07	Phosphorus.....P	31.04
Carbon.....C	12.005	Platinum.....Pt	195.2
Cerium.....Ce	140.25	Potassium.....K	39.10
Cesium.....Cs	132.81	Praseodymium.....Pr	140.9
Chlorine.....Cl	35.46	Radium.....Ra	226.0
Chromium.....Cr	52.0	Rhodium.....Rh	102.9
Cobalt.....Co	58.97	Rubidium.....Rb	85.45
Columbium.....Cb	93.1	Ruthenium.....Ru	101.7
Copper.....Cu	63.57	Samarium.....Sa	150.4
Dysprosium.....Dy	162.5	Scandium.....Sc	45.1
Erbium.....Er	167.7	Selenium.....Se	79.2
Europium.....Eu	152.0	Silicon.....Si	28.1
Fluorine.....F	19.0	Silver.....Ag	107.88
Gadolinium.....Gd	157.3	Sodium.....Na	23.00
Gallium.....Ga	70.1	Strontium.....Sr	87.63
Germanium.....Ge	72.5	Sulfur.....S	32.06
Glucinum.....Gl	9.1	Tantalum.....Ta	181.5
Gold.....Au	197.2	Tellurium.....Te	127.5
Helium.....He	4.00	Terbium.....Tb	159.2
Holmium.....Ho	163.5	Thallium.....Tl	204.0
Hydrogen.....H	1.008	Thorium.....Th	232.15
Indium.....In	114.8	Thulium.....Tm	169.9
Iodine.....I	126.92	Tin.....Sn	118.7
Iridium.....Ir	193.1	Titanium.....Ti	48.1
Iron.....Fe	55.84	Tungsten.....W	184.0
Krypton.....Kr	82.92	Uranium.....U	238.2
Lanthanum.....La	139.0	Vanadium.....V	51.0
Lead.....Pb	207.20	Xenon.....Xe	130.2
Lithium.....Li	6.94	Ytterbium(Neoytterbium)Yb	173.5
Lutecium.....Lu	175.0	Yttrium.....Yt	89.32
Magnesium.....Mg	24.32	Zinc.....Zn	65.4
Manganese.....Mn	54.93	Zirconium.....Zr	90.0
Mercury.....Hg	200.6		

<sup>5</sup> Baxter and Parsons, THIS JOURNAL, 43, 507 (1921).

In addition to the changes noted above, the value for silicon due to Baxter, Weatherill and Holmes, which was cited in our last report, namely,  $Si = 28.111$  may be adopted now and rounded off to 28.1.

(Signed) F. W. CLARKE.

T. E. THORPE.

G. URBAIN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

## SOLUBILITIES IN MIXTURES OF TWO SOLVENTS.

BY GEORGE PUCHER AND WILLIAM M. DEHN.

Received May 29, 1920.

In a recent paper<sup>1</sup> by one of us on solubilities in mixtures of water and pyridine, it was stated<sup>2</sup> that more extensive and accurate solubility studies of pyridine, quinoline, etc. are to be made, also efforts will be made to prepare the molecular compounds indicated. This paper includes studies of solubilities both in mixtures of water and pyridine and in mixtures of alcohol and quinoline; and the molecular compound  $C_9H_7N \cdot 3CO-(NH_2)_2$ , indicated by the curve of solubilities of urea in the alcohol-quinoline mixtures, was isolated and studied.

Although constants of solubility are the most numerous and useful of chemical data, and although solutions themselves afford the media of the vast majority of chemical reactions, little is accurately known concerning either the nature of solutions or the mechanism of chemical reactions in solutions. It is true that the nature of solutions has been studied deeply from the standpoints of the phase rule, the kinetic theory, and the ionic theory, yet it can scarcely be held that the intimate nature of solvent and solute has thereby been elucidated. Cryoscopic and ebullioscopic methods have recently demonstrated the frequent existence in solution of molecular compounds aggregated of the solvent and the solute, and other physical methods have confirmed these demonstrations, but all methods failed, except rarely, to yield the molecular compound itself.

In the present and the earlier paper, the existence of the molecular compound is not only indicated by the solubility curve but the method of mixed solvents can yield the molecular compound itself. For these reasons, and because the method possesses simplicity and ease of application, it is planned to undertake other investigations with mixed solvents, the main objects of which are to study the general problem of solubility, to demonstrate that curved or broken lines of solubility indicate the formation of molecular compounds, and to separate the molecular compounds when possible.

<sup>1</sup> THIS JOURNAL, 39, 1399 (1917).

<sup>2</sup> *Ibid.*, 39, 1404 (1917).

It has been assumed that straightness of line of plotted solubilities indicates a purely physical relation of solute and solvent. This assumption is confirmed by studying the solubilities of hydrated and non-hydrated salts. The former yield curved or broken lines; the latter yield straight or nearly straight lines. Since the latter can be accounted for by a mere physical mingling of solute and water molecules, the former can be, and presumably are, accounted for by states of hydration, that is, by the formation of molecular compounds.

The existence of the most varied types of other molecular compounds in solution is set forth in the literature. These compounds have, however, only rarely been studied in connection with solubility.<sup>3</sup> The lack of study along this line may be explained by the fact that ordinary solubility is conditioned by concentration and temperature and that rising temperature decomposes the molecular compound if present. In studies of solubility in mixed solvents, however, any desired low temperature can be employed and observations and data, not possible by the former method, are obtainable.

### Experimental.

Commercial pyridine was dried with solid potassium hydroxide and metallic sodium, and distilled. The quinoline was freed from nitrobenzene and aniline and then was dehydrated by the same method. Commercial "absolute" alcohol was dehydrated by treatment with calcium carbide and then was distilled into vessels kept free from atmospheric moisture. The materials studied as solutes were taken from the usual laboratory stock and for the most part were not purified.

The determinations of solubilities, unless otherwise stated, were made at the room temperatures of 20° to 25°. The solubilities are largely expressed as grams of solute in 100 g. of the solvent. Excess of the solute and about 5 cc. of the solvent were enclosed in a small vial; the mixture was shaken vigorously or was allowed to stand until equilibrium was established. The solution was then filtered rapidly into a weighed crucible and the latter with contained solution was weighed as quickly as possible. After drying *in vacuo* or on a water-bath, the crucible was again weighed. The weight of the residue and of the solvent lost yielded the desired data. No high degree of accuracy is claimed for the solubilities given in Table I, because merely a preliminary survey of the field was made in order to find compounds behaving abnormally in the alcohol-quinoline mixture.

The first column indicates solubilities in absolute alcohol; the second, in equimolecular mixture of alcohol and quinoline; the last, in absolute quinoline. The plus sign given with the figures indicates that the solute

<sup>3</sup> The limited bibliography on solubilities of organic compounds in mixed solvents is indicated in the former paper. Ref. 1.



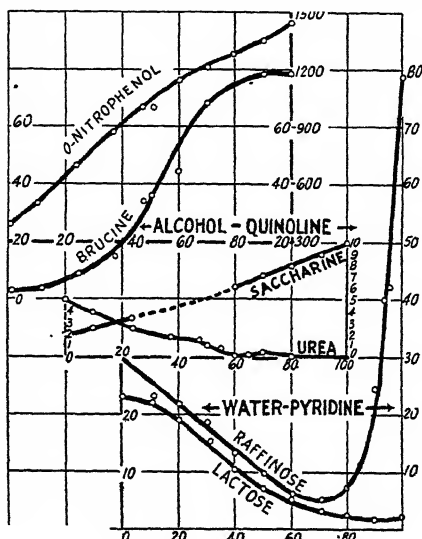
had partially volatilized; the  $\infty$  sign indicates that only a solid phase had formed.

TABLE I.

## SOLUBILITIES IN MIXTURES OF ALCOHOL AND QUINOLINE.

Solute.	Alcohol.	Equimolecular mixture.	Quinoline.
Acetamide	31.50	.....	.....
Acetanilide	21.30	23.69	12.67
Antipyrine	74.09	36.55+	19.00+
Asparagine	0.02	0.18	0.11
Azobenzene	9.29	22.88+	.....
Benzamide	17.03	18.55+	6.27+
Benzidine	7.68+	47.23+	43.07+
Borneol	175.50	.....	.....
Brucine	2.35	43.51	79.00
Caffeine	1.88	3.93	3.56
Carbazole	1.30	9.86	33.40
Casein	0.28	0.92	0.38
Chloral hydrate	215.00	0.58+	12.56+
Cinnamic acid	22.03	132.40	1.85+
Coumarine	12.57	0.80+	0.56+
Diphenyl urea	0.84	3.12	2.50
Ethyl urea	79.95	5.55+	1.13+
Glycocoll	0.06	0.17	0.07
Hemoglobin	0.37	0.59	0.23
Hippuric acid	4.60	23.10	20.41
Hydrobenzamide	1.99	2.56	3.94
Indol	35.85	12.00	11.39
Lactose	0.09	1.32	1.96
Michler's ketone	0.63	6.86	9.72
Naphthalene	9.80	4.69	3.02
Nitrobenzaldehyde	22.14	7.07+	1.96+
<i>o</i> -Nitrophenol	404.00	1000.00	1450.00
<i>m</i> -Nitrophenol	.....	.....	$\infty$
<i>p</i> -Nitrophenol	.....	$\infty$	.....
Papaverine	.....	.....	7.66
Phenacetin	18.80	12.87	7.83
Phenolphthalein	10.24	0.19	0.32
Piperine	6.66	18.81	13.66
Quinine	166.60	30.04	22.28
Raffinose	3.60	5.04	.....
Resorcinol	236.00	99.81+	$\infty$
Saccharine	2.00	.....	10.10
<i>p</i> -Toluidine	110.00	.....	.....
Trilaurine	6.66	16.57	18.22
Tristerine	13.00	$\infty$	5.35
Urea	5.00	$\infty$	0.11
Urethane	96.70	.....	9.72+
Uric acid	0.68	0.61	1.13
Vanillin	67.22	64.30	5.51
Xyloquinone	1.12	4.69	3.02

It will be observed in many cases that the solubilities in the mixtures of the two solvents are often either higher or lower than the solubilities in the respective pure solvents. These peculiarities are most marked in the cases of urea, saccharine, *p*-nitrophenol, acetanilide, resorcinol, piperine, cinnamic acid, and chloral hydrate. The first three gave definite



evidences of molecular-compound formation, either by the evolution of heat in mixing, or by the solidifying of the solutions at certain concentrations, or from the form of the curves obtained. Six compounds were studied in selected concentrations of mixed solvents and the data obtained are given in Tables II and III.

TABLE II.  
SOLUBILITIES IN MIXTURES OF ALCOHOL AND QUINOLINE.

%C <sub>2</sub> H <sub>5</sub> N.	Urea.	Saccharine.	Brucine.	<i>o</i> -Nitrophenol.
0.0	5.00	2.00	3.50	404
10.0	4.00	2.50	3.86	504
23.2	2.50	3.30	10.87	720
37.5	1.80	....	15.09	864
47.5	1.50	....	34.60	1008
50.0	1.05	....	36.50	1005
55.0	0.64	....	....	....
60.0	0.26	6.00	44.60	1152
65.0	0.32	....	....	....
70.0	0.50	7.01	68.20	1224
80.0	0.19	8.05	75.00	1296
90.0	0.10	8.80	78.70	1367
100.0	0.11	10.10	79.00	1450

The urea was estimated by the hypobromite method. The *o*-nitrophenol was estimated colorimetrically in 10% sodium hydroxide solution.

The solubilities of these, therefore, are expressed as grams of solute in 100 cc. of solutions.

TABLE III.  
SOLUBILITIES IN MIXTURES OF WATER AND PYRIDINE.

% C <sub>6</sub> H <sub>5</sub> N.	Lactose at 1°.	Lactose at 25°.	Raffinose at 25°.
0.0	19.18	23.04	29.83
10.0	17.84	22.35	23.12
20.0	15.29	19.24	22.16
30.0	12.93	15.48	18.88
40.0	9.48	10.56	13.42
50.0	6.87	7.75	9.94
60.0	4.61	5.62	6.51
70.0	2.85	3.22	5.32
80.0	1.62	2.62	7.40
81.4	2.22	2.50	4.49
90.0	1.75	1.77	24.50
91.0	1.83	1.82	24.60
92.0	....	....	24.70
94.0	....	....	36.90
96.0	....	....	41.90
98.0	....	....	45.70
100.0	1.61	2.22	79.08

It will be observed that the solubilities of urea decrease quite regularly as the concentrations of quinoline increase, but at 60% a definite break occurs. At this concentration a molecular compound is formed, as shown by the following method of its preparation.

**Quinoline Tri-urea.**—To 100 cc. of absolute alcohol, sufficient urea was added to saturate at room temperature, then 110 cc. of quinoline was added while the mixture was shaken vigorously. The precipitate first formed was dissolved by gentle warming; on cooling to room temperature and standing for some hours, a white crystalline mass separated. It was filtered and washed with absolute ether. To be certain that the product contained no free urea, it was redissolved by warming in a 60% solution of quinoline in alcohol, and a little alcohol was added. The volume of the latter used was made sufficient to yield on cooling and standing only about one-half of the original precipitate. In this manner short, snow-white needles were obtained. After washing with absolute ether and drying in a desiccator, these crystals gave 31.50% of N. Calc. for C<sub>9</sub>H<sub>7</sub>N<sub>3</sub>CO(NH<sub>2</sub>)<sub>2</sub>: N, 31.70%.

Quinoline tri-urea softens at 150° and melts<sup>4</sup> at 154°. It is insoluble in ether, is easily soluble in alcohol and in hot 60% quinoline solution in alcohol. In moist air it gives off the odor of quinoline; in water it yields an oily layer of quinoline; its ready hydrolysis is indicated here. When heated above 45° ammonia<sup>4</sup> is evolved; at quite elevated temperatures, quinoline is given off. Since quinoline tri-urea and its decomposition products do not yield violet colored salts or solutions with copper sulfate, it is concluded that they do not possess a cyanuric or a biuret structure.

**Quinoline tri-urea chloroplatinate.**—This compound was formed when quinoline tri-urea, dissolved in absolute alcohol, was treated with an alcoholic solution of platinum chloride. The yellow amorphous precipitate upon recrystallization from hot water gave glistening orange needles.

<sup>4</sup> Urea melts at 132° and gives off ammonia only above 110°.

*Analyses.* Calc. for  $C_9H_7N_3CO(NH_2)_2.PtCl_4$ : Pt, 30.00; Cl, 22.01; Found: Pt, 30.07; Cl, 22.26.

This chloroplatinate is quite stable toward hot water, but with alkalis it easily yields free quinoline.

Substituted ureas, such as ethyl urea, diethyl urea, phenyl urea, did not yield by the above method molecular compounds with quinoline. Urea and pyridine also failed to yield a molecular compound.

**Saccharine in Alcohol and Quinoline.**—When the mixtures contained between 20 and 60% of quinoline, they evolved heat and solidified completely. Above 60% concentration, heat was produced and a liquid only was obtained. The indicated molecular compound of saccharine and quinoline was not isolated.

**Brucine in Alcohol and Quinoline.**—The character of this curve indicates a molecular compound. It was not isolated.

**The Nitrophenols in Alcohol and Quinoline.**—The three isomers reveal marked differences.<sup>5</sup> The *para* form gives only a solid in the equimolecular mixture of the two solvents; the *meta* form gives only a solid in pure quinoline; the *ortho* form gives a solubility curve that is nearly straight.

**Lactose in Water and Pyridine.**—The solubility curve indicates the probable formation in solution of a molecular compound.

**Raffinose in Water and Pyridine.**—A remarkable curve was obtained in these solutions and indicates the probable formation of a molecular compound. The original raffinose did not reduce copper solutions; the residues from the solutions, especially those near the 50–50% concentrations did reduce somewhat; the solutions themselves showed little or no reduction. This curve and other problems suggested by this paper will be investigated farther.

### Summary.

In mixtures of alcohol and quinoline and in mixtures of pyridine and water, certain solutes yielded solubility data indicating or demonstrating molecular compounds. Studies of solubilities in mixed solvents seem to offer a convenient method of study of additive tendencies of solute and solvent.

SEATTLE, WASH.

<sup>5</sup> It was shown by Kerryman (*Ber.* 39, 1022 (1906)) that *ortho* substituted benzene derivatives form additive compounds much less readily than the *meta* and *para* derivatives. Our data confirm this conclusion.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA.]

## A FURTHER INVESTIGATION OF THE VELOCITY OF SUGAR HYDROLYSIS.

By R. H. CLARK.

Received November 22, 1920.

The hydrolysis of cane sugar has been found by most investigators to be monomolecular with respect to sugar. If the amount of water is relatively large the velocity coefficient should be independent of the initial concentration of the sugar, according to the equation of mass action. Ostwald,<sup>1</sup> however, found that the velocity coefficient increased rapidly with the concentration of the sugar. For example, using a 0.5 *N* hydrochloric acid solution as catalyzer he found the inversion coefficient to be 20.63 for a 10% sugar solution, 22.87 for 20% and 29.16 for a 40% solution.

E. Cohen<sup>2</sup> attributed the phenomenon to the fact that the volume of the reaction is reduced the greater the concentration of the sugar and hence the number of collisions between the molecules of sugar and the hydrogen ions is increased, causing an increase in the velocity of the reaction.

That this latter view was correct was experimentally demonstrated by Rosanoff, Clark and Sibley,<sup>3</sup> by preparing three pairs of solutions, in which the acid and water had exactly the same concentration in each pair, but the sugar in one solution of each pair was replaced, in part, by glucose. Preliminary experiments were carried out to find how much glucose must be added in place of part of the cane sugar in order to keep the volumes equal. For example, in one of the pairs containing (a) 50.500 g. of cane sugar, 195.73 g. of water and 28.750 g. of formic acid in 250 cc., and (b) 14.250 g. of cane sugar, 35.00 g. of glucose, 195.73 g. of water and 28.750 g. of formic acid in 250 cc., the velocity constants of the monomolecular mass-law equation were identical, although the initial concentrations of cane sugar were in the ratio of 3.54 to 1. More recently the present writer has confirmed this result using a strong acid, hydrochloric, as catalyzer. The velocity of cane sugar hydrolysis therefore is independent of the initial concentration of the sugar when the concentrations of both acid and water are constant. Consequently the following measurements were made, to find whether in a similar manner, adding an inert substance, glucose, to keep the concentration of the water and cane sugar constant while varying the concentration of the acid, would have an appreciable effect in yielding a numerical proportionality between the quantity of hydrogen ions present and the inversion velocity.

<sup>1</sup> Ostwald, *J. prakt. Chem.*, 31, 316 (1885).

<sup>2</sup> E. Cohen, *Z. physik. Chem.*, 23, 442 (1897).

<sup>3</sup> Rosanoff, Clark and Sibley, *THIS JOURNAL*, 33, 1911 (1911).

It has long been known that there is only an approximate proportionality between the quantity of hydrogen ions and the inversion velocity of cane sugar. For example, in the case of hydrochloric acid, Ostwald found that a 0.5 *N* solution inverts 6.14 times more quickly than a 0.1 *N* solution and 64.66 times more quickly than a 0.01 *N*, although the 0.5 *N* solution contains only 4.65 times as many hydrogen ions as the 0.1 *N* and 44.73 times as many as the 0.01 *N*, as measured by the conductivity method.<sup>4</sup>

A theory to account for this variation was advanced by Arrhenius, namely, that the catalytic activity of hydrogen ions is greatly stimulated by the presence of other ions. More recently Bredig,<sup>5</sup> Acree,<sup>6</sup> Snethlage,<sup>7</sup> McBain and Coleman<sup>8</sup> and others, have advanced much evidence to show that the catalytic effect of the acid in this and other similar catalytic reactions is produced partly by the ions and partly by the undissociated acid.

In the experiments summarized below, the extent of hydrolysis was measured with a half-shade quartz-wedge compensation saccharimeter. The reaction mixtures were maintained at a temperature of 25° ± 0.02°. The rotations were observed at the same temperature as nearly as possible, the saccharimeter being enclosed in a wooden box for this purpose. Merck's glucose, after having been recrystallized three times from 95% alcohol, was used.

The measuring flasks were calibrated at 25° and the amount of glucose to be employed as space filler was obtained by preliminary experiments at this same temperature. All reaction mixtures containing glucose were allowed to stand until its rotation became constant before mixing. The cane sugar, glucose and exact weight of water needed for each experiment were put in a measuring flask and the acid in a glass-stoppered bottle; they were kept in the thermostat, and finally thoroughly and quickly mixed.

The inversion velocities of the following reaction mixtures were measured to find the effect of keeping the concentration of the water and sugar constant while varying the concentration of the respective acids employed as catalyzer. This was done by adding glucose to the weaker acid solutions to fill up the volume occupied by the acid removed.

In the tables, *t* denotes the time in hours,  $\alpha$  the observed rotation, and *k* the velocity constant calculated from the monomolecular equation  $k = \frac{1}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}$ ,  $\alpha_0$  and  $\alpha_\infty$  denoting the initial and final rotations, respectively. The initial rotations (*t* = 0) were not observed but calculated by plotting on a large scale, the available values of  $\log (\alpha - \alpha_\infty)$  and extrapolating to *t* = 0, to find  $\log (\alpha_0 - \alpha_\infty)$  and hence  $\alpha_0$ .

<sup>4</sup> From equivalent conductances, Whetham's "Theory of Solution." 1902, Cambridge University Press.

<sup>5</sup> Bredig, *Ann. Reports Chem. Soc.*, 1914, p. 16.

<sup>6</sup> Acree, *Am. Chem. J.*, 49, 353 (1913).

<sup>7</sup> Snethlage, *Z. physik. Chem.*, 85, 255 (1913).

<sup>8</sup> McBain and Coleman, *J. Chem. Soc. Trans.*, [II] 105, 1517 (1914).

## REACTION MIXTURES.

In each case 57 g. of cane sugar was used. The total volume was 250 cc.

Solution.	Water, g.	Acid, g.	N.	Glucose, g.
I	212.89	4.5562	HCl(0.5 )	....
II	212.89	0.9112	(0.1 )	2.40
III	212.89	0.0911	(0.01)	2.95
IV	211.35	7.875	HNO <sub>3</sub> (0.5 )	....
V	211.35	1.575	(0.1 )	4.40
VI	211.35	0.1575	(0.01)	5.40
VII	211.99	10.125	HBr(0.5 )	....
VIII	211.99	2.025	(0.1 )	3.63
IX	211.99	0.2025	(0.01)	4.44
X	212.77	6.125	H <sub>2</sub> SO <sub>4</sub> (0.5 )	....
XI	212.77	1.225	(0.1 )	2.595
XII	212.77	0.1225	(0.01)	3.18

The results for the hydrochloric acid solutions only are tabulated in full, in Tables I-III; the inversion velocity constants for the other reaction mixtures are given in Table IV.

TABLE I.

<i>t</i> .	$\alpha$ .	<i>k</i> .
0.0	89.3°	.....
0.25	79.3	0.1556
0.50	70.3	0.1544
0.83	59.5	0.1537
1.	54.2	0.1554
1.25	47.4	0.1545
1.5	41.2	0.1539
2.	29.4	0.1564
2.5	19.8	0.1572
3.	11.9	0.1575
4.	-0.3	0.1585
5.	-8.4	0.1576
6.5	-16.3	0.1571
$\infty$	-27.4	.....

Av. 0.156

TABLE II.

<i>t</i> .	$\alpha$ .	<i>k</i> .
0.0	(91.7°)	.....
0.25	89.9	0.0276
0.50	86.7	0.0255
0.83	81.9	0.0255
1.	73.0	0.0253
1.25	62.1	0.0255
1.5	48.2	0.0254
2.	36.3	0.0255
2.5	26.7	0.0253
3.	-24.9	.....
4.		-----
5.	Av.	0.0255

TABLE III.

<i>t</i> .	$\alpha$ .	<i>k</i> .
0.0	(91.8°)	.....
0.25	91.6	0.0028
1.	91.1	0.0026
5.	88.8	0.0023
11.	85.0	0.0024
29.	74.4	0.0024
53.	61.8	0.0025
99.	41.9	0.0025
$\infty$	-24.0	.....
	Av.	0.0025

TABLE IV.

Solution.	N, Acid.	Inversion coefficient.
IV	0.5 HN <sub>3</sub> O <sub>4</sub>	0.154
V	0.1	0.0252
VI	0.01	0.0024
VII	0.5 HBr	0.169
VIII	0.1	0.0260
IX	0.01	0.00245
X	0.5 H <sub>2</sub> SO <sub>4</sub>	0.0797
XI	0.1	0.0157
XII	0.01	0.0020

The results show, for example, that the 0.5 N hydrochloric acid solution

inverts the cane sugar with a velocity 6.11 times as great as the 0.1 *N* and 62.36 times as great as does the 0.01 *N* solution. The results with the other acids are similar; in no case, does the expedient of adding an inert substance, glucose, in order to keep the concentration of the water and cane sugar constant while varying the concentration of the acid, produce any appreciable effect in yielding a numerical proportionality between the quantity of hydrogen ions employed as catalyzer and the inversion velocities.

Fairly wide differences for the degree of dissociation of the various acids have been used by various investigators, in calculating the catalytic effect of the hydrogen ions and the undissociated part of the acid. For purposes of comparison with the results obtained by Marshall<sup>9</sup> from Ostwald's sugar inversion measurements, the degrees of dissociation of hydrochloric, nitric and hydrobromic acids employed by him, have been used in calculating from the above measurements, the values of  $K_m$  and  $K_i$ , and the ratio  $K_m / K_i$ , which is the ratio between the catalytic effect of undissociated acid and that of an equal concentration of hydrogen ions. From the values of  $K_m$  and  $K_i$  obtained,  $K_m$  the molecular inversion velocity for the different concentrations has been calculated for comparison with that experimentally found.

#### HYDROCHLORIC ACID AND SUGAR.

Conc. of acid, <i>N</i> .	$\alpha$ .	$K_m = 0.632 \quad K_i = 0.236.$		
		$K_m / K_i$ .	$K_n$ found.	$K_n$ calc.
0.5	0.809	2.67	0.312	0.312
0.1	0.953	....	0.255	0.255
0.01	1.000	....	0.250	0.236

#### NITRIC ACID AND SUGAR.

$K_m = 0.626 \quad K_i = 0.233.$				
0.5	0.811	2.68	0.308	0.308
0.1	0.953	....	0.252	0.252
0.01	1.000	....	0.240	0.234

#### HYDROBROMIC ACID AND SUGAR.

$K_m = 0.768 \quad K_i = 0.234.$				
0.5	0.805	3.28	0.338	0.338
0.1	0.951	....	0.260	0.260
0.01	1.000	....	0.245	0.235

#### SULFURIC ACID AND SUGAR.

$K_m = 0.179 \quad K_i = 0.144.$				
0.5	0.550	1.244	0.1598	0.1594
0.1	0.620	....	0.1574	0.1570
0.01	0.850	....	0.1522	0.1600

The value of  $\alpha$  for 0.5 *N* sulfuric acid was calculated from the equivalent conductances as given by Kohlrausch<sup>4</sup> for a temperature of 18° after

<sup>9</sup> Marshall, *Am. Chem. J.*, 49, 353 (1913).



being corrected to 25° by Jones'<sup>10</sup> temperature coefficient. The values for the other two concentrations are the average given by Noyes.<sup>11</sup>

The agreement between the calculated and found values of  $K_n$  is of the same order as that calculated by Marshall from Ostwald's measurements. The values of  $K_i$  for the hydrogen ion, from the first three acids are the same, ( $K_i = 0.234$ ) but for sulfuric acid has fallen to  $K_i = 0.144$ . Likewise the activity of the nonionized acid, which is from 2.6 to 3.3 times that of the hydrogen ions for the three acids, hydrochloric, nitric and hydrobromic, is in the case of sulfuric only 1.24 times as great.

### The Effect of Neutral Salts.

Analogous experiments were carried out to find the comparative effect produced on the rate of inversion by a strong acid (Solution XIII), a strong acid together with a neutral salt containing a common ion (Solution XIV), and a strong acid together with an inert substance, glucose (Solution XV), the glucose occupying the same volume as the neutral salt in the preceding series. In this series also 57 g. of cane sugar was used, and the volume was 250 cc. In each solution the weight of nitric acid was 0.7875 g.

Solution.	Water.	KNO <sub>3</sub> .	Glucose.
XIII	214.36	.....	....
XIV	198.46	10.1100	....
XV	198.46	.....	6.89

Solution XIII.			Solution XIV.			Solution XV.		
<i>t</i> .	$\alpha$ .	<i>k</i> .	<i>t</i> .	$\alpha$ .	<i>k</i> .	<i>t</i> .	$\alpha$ .	<i>k</i> .
0.0	(88.6°)		0.0	(88.2°)		0.0	(95.8°)	
0.25	87.0	0.0212?	0.75	85.4	0.0141	0.25	94.9	0.0136?
3.	78.7	0.0128	1.5	82.6	0.0144	0.75	93.3	0.0127
6.	70.4	0.0123	3.	77.3	0.0143	1.5	90.9	0.0125
11.	57.7	0.0122	8.	61.4	0.0142	3.	86.2	0.0125
19.	40.7	0.0124	16.	40.0	0.0141	6.	77.4	0.0126
29.	23.9	0.0122	25.	23.1	0.0143	10.	67.0	0.0125
37.	13.5	0.0122	33.	11.2	0.0143	13.	60.0	0.0124
47.	3.1	0.0123	43.	0.6	0.0142	23.	40.1	0.0124
55.	-3.2	0.0123	51.	-6.0	0.0142	30.0	28.5	0.0125
75.	-14.1	0.0124	$\infty$	-27.7		46.	10.5	0.0126
$\infty$	-27.8	.....				$\infty$	-20.2	.....
Av. 0.0123			Av. 0.0142			Av. 0.0125		

The effect produced on the inversion velocity by an amount of glucose occupying the same volume as the potassium nitrate is seen to be very slight. The increase in velocity produced by the neutral salt can to a very

<sup>10</sup> Jones, "Electrical Conductance," etc. *Carnegie Inst. Pub.*, 1912, p. 170.

<sup>11</sup> Noyes, "The Electrical Conductance of Aqueous Solutions," A. A. Noyes, *ibid.*, 63, 268 (1907).

little extent therefore be attributed to the fact that the volume of reaction mixture is reduced by the presence of the neutral salt. This is in agreement with the conclusions arrived at by McBain and Coleman,<sup>12</sup> who have shown in a number of cases that if the catalytic effect of the undissociated acid formed in the presence of neutral salts be taken into account the velocities of inversion are within 4% of the predicted rates.

### Summary.

The addition of an inert substance, to keep the concentration of water and cane sugar constant while varying the concentration of the acid, has no appreciable effect in producing a numerical proportionality between the quantity of hydrogen ions present and the inversion velocity of cane sugar.

The increase in velocity of cane sugar hydrolysis produced by a strong acid in the presence of a neutral salt of that acid, over the velocity produced by that acid alone, can to very little extent be attributed to the fact that the volume of the reaction is reduced by the presence of the salt.

On the assumption that both the undissociated and dissociated forms of an acid are catalytically active in cane sugar inversion, the values of  $K_i$  for the hydrogen ion from hydrochloric, hydrobromic and nitric acids have the same value ( $K_i=0.234$ ); the corresponding value for sulfuric acid is considerably lower ( $K_i=0.144$ ).

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[ CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH. ]

## THE VISCOSITY OF GELATIN SOLS.

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Received January 3, 1921.

### Introduction.

A mathematical expression for the viscosity of two-phase systems was developed by A. Einstein<sup>2</sup> in 1906 and generalized by E. Hatschek<sup>3</sup> in 1910-1913. According to the latter investigator, the viscosity of all two-phase systems may fall in one of two possible conditions. So long as the particles of dispersed phase occupy so small a proportion of the total volume of the system that they do not touch each other, the increase of viscosity should be a linear function of the concentration only and independent of the size of the particles. In the derivation of his formula, the particles of dispersed phase are assumed to be spherical, undeformable, and

<sup>12</sup> McBain and Coleman, *J. Chem. Soc.*, [II] 105, 1523 (1914).

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<sup>2</sup> A. Einstein, *Ann. Physik.*, 19, 289 (1906).

<sup>3</sup> E. Hatschek, *Kolloid, Z.*, 7, 301 (1910); 8, 34 (1911); *Trans. Faraday Soc.*, 9, 80 (1913).

of smooth surface. These conditions are probably seldom attained, but a reasonable conformity to his formula has been found in the case of gamboge and mastic by Bancelin,<sup>4</sup> and in the case of starch by Harrison.<sup>5</sup>

Hatschek writes the equation,

$$\eta' = \eta (1 + 4.5 f) \quad (1)$$

when  $\eta'$  is the viscosity of the system,  $\eta$  the viscosity coefficient of the liquid or continuous phase, and  $f$  the ratio of the volume of the dispersed phase to the total volume of the system. The constant 4.5 has been given several different values, however, by different observers. Einstein first gave it a value of unity, and later changed it to 2.5. Bancelin found it to be 2.9.

Just as soon, however, as the ratio of the volume of the dispersed phase to the total volume of the system becomes so great that the particles touch each other, then the viscosity-concentration curve no longer remains linear, but becomes curvilinear. (The volume of the dispersed phase, as here used, includes the sum of the volume of the dispersed particles *per se* and the volume of the liquid or dispersion medium which has become associated with the dispersed particles in a solvated or hydrated condition.) The volume of the dispersed phase at the moment when the above condition is attained will be 74.04% of the total volume, according to Hatschek's calculations, and as the concentration becomes greater, the previously spherical particles will, in the case of an emulsion and an emulsoid at least, become dodecahedral; and if the system is now subjected to shear it will quickly assume a position in which such shear will take place entirely in the continuous phase. Under these new conditions, the viscosity is expressed by

$$\eta = (\sqrt[3]{A} / \sqrt[3]{A - 1})^3 \quad (2)$$

in which  $\eta$  is the coefficient of viscosity of the system, and  $A$  is the ratio of the total volume of the system to the volume of the dispersed phase. As we are unable directly to measure the volume of the dispersed phase of an emulsoid, we may obtain the value of  $A$  by a rearrangement of Equation 2; thus,

$$A = (\eta / (\eta - 1))^3, \quad (3)$$

and if the amount of dispersed substance is expressed in percentage, *e. g.*, total volume divided by dispersed weight, then this value, which Hatschek calls  $A'$  should bear a constant ratio to  $A$  which is total volume divided by the dispersed volume, or  $A' / A = K$ .

<sup>4</sup> Bancelin, *Kolloid Z.*, 9, 154 (1911).

<sup>5</sup> Harrison, *J. Soc. Dyers Colorists*, 27, 84 (1911).

This has been tested by Hatschek using the data of Botazzi and d'Errico<sup>6</sup> upon glycogen sol, and of Chick and Martin<sup>7</sup> upon sodium caseinogenate sol. Hatschek finds the value of  $K$  to be nearly constant at about 2.1 between the concentrations of 30 and 45 in the glycogen sol, and at about 9.5 between the concentrations of 6.04 and 9.39 in the case of the casein sol.

As expressions of the type developed by Hatschek are fundamental and must inevitably lead to a better understanding of the complex conditions obtaining in colloid sols, it becomes desirable that experimental data be accumulated which will tend either to confirm the hypotheses upon which the formulas are based, or to indicate points which will require mathematical revision. With this end in view, the following experiments have been conducted upon gelatin sols.

### Experimental.

A high grade of gelatin was used in concentrations varying by small increments from 0.01 to 30.00%. In order that comprehensive data might be obtained the viscosity of gelatin in five different conditions was studied. In Series 1 the gelatin was dissolved in distilled water giving a solution whose hydrogen-ion value in 1% concentration was  $1.5 \times 10^{-6}$ , so that the solute was essentially calcium gelatinate. In Series 2, an iso-electric gelatin was obtained by screening gelatin powder, taking that portion which passed a 40-mesh screen but was retained by one of 60 mesh, soaking it for an hour in hydrochloric acid of 0.0078  $N$  concentration, filtering, and washing several times with distilled water. A 1% solution had a hydrogen-ion concentration of  $2 \times 10^{-5}$ , the value of gelatin at its iso-electric point. Series 3 was treated in a similar way to the preceding, except that the acid used was of 0.031  $N$  concentration. It had previously been found that such treatment resulted in the maximum of swelling and of viscosity, while at the iso-electric point these properties possessed their minimum values. Series 4 and 5 were treated similarly to Series 2 and 3 respectively, except that the acids in which they were allowed to soak were not removed, but the gelatin was dissolved and diluted to the desired concentration in the presence of the large excess of acid.

The temperature selected for all determinations was fixed at 35° in order that no complications due to an equilibrium between what Smith<sup>8</sup> calls sol form *A* and gel form *B* should arise. At 35° the gelatin is, according to Smith, entirely in the condition of the sol form *A*. The temperature was maintained constant by the immersion of all samples and appa-

<sup>6</sup> Botazzi and d'Errico, *Pfluger's Arch.*, **115**, 359 (1906).

<sup>7</sup> Chick and Martin, *Kolloid Z.*, **11**, 102 (1912).

<sup>8</sup> C. R. Smith, *THIS JOURNAL*, **41**, 135 (1919); *J. Ind. Eng. Chem.*, **12**, 878 (1920).

ratus in a thermostat, the average fluctuation of which was  $\pm 0.05^\circ$  at  $35^\circ$ .

All viscosity measurements, with three exceptions, were made by the use of an Ostwald capillary viscosimeter, employing 3 cc. for each determination. Duplicate runs were made in each case, and the average used in the calculations. The variation between duplicate measurements was rarely more than 0.2 to 0.3 second, even in the more viscid concentrations. The viscosity of Expts. 23, 24 and 25 of Series 1 was measured by the use of a MacMichael viscosimeter.

The data obtained are given, in part, in the following tables. The first column of Table I shows the percentage concentration,  $C$ , of the gelatin sol; in Col. 2 is given the coefficient of viscosity, water being taken as unity; in Col. 3 the values calculated for  $A$  by Equation 3; in Col. 4 the value for  $A'$ , *e. g.*, 100 divided by dispersed weight in percentage; and in Col. 5 the ratio of  $A'/A$ . The remaining two columns will be discussed later.

TABLE I.

## SERIES 1.

NORMAL GELATIN,  $1.5 \times 10^{-3}$ .

$C$ .	$\eta/\eta_w$ .	$A$ .	$A'$ .	$K$ .	$V_m$ .	$k_s$ .
0.05	1.023	....	....	....	....	....
0.10	1.045	....	....	....	....	....
0.20	1.073	....	....	....	....	....
0.40	1.124	....	....	....	....	....
0.60	1.211	....	....	....	....	....
0.80	1.328	....	....	....	....	....
1.00	1.404	42.2	100.0	2.37	....	....
1.50	1.522	24.9	66.66	2.68	....	....
2.00	1.818	11.0	50.00	4.54	....	....
2.50	2.100	7.00	40.00	5.72	....	....
3.00	2.400	5.08	33.33	6.55	....	....
3.50	2.740	3.94	28.58	7.25	....	....
4.00	3.078	3.27	25.00	7.64	....	....
4.50	3.475	2.78	22.12	7.95	64.2	8.46
5.00	4.125	2.32	20.00	8.62	56.8	8.97
6.00	5.970	1.74	16.66	9.57	42.6	9.57
7.00	7.430	1.56	14.28	9.16	35.8	9.36
8.00	9.550	1.40	12.50	8.92	28.6	9.36
9.00	11.82	1.31	11.11	8.48	23.6	9.11
10.00	15.62	1.23	10.00	8.13	18.7	8.97
11.00	19.40	1.18	9.09	7.71	15.1	8.73
12.00	23.45	1.15	8.33	7.24	13.1	8.38
15.00	29.00	1.12	6.66	5.95	10.8	7.23
20.00	63.00	1.08	5.00	4.63	7.4	6.17
30.00	800.00	1.013	3.33	3.28	1.6	5.60

In Table II are shown the values obtained for  $K$  and for  $k_s$  for the five series.

TABLE II.

COMPARISON OF VALUES OF  $K$  AND  $k_s$  FOR THE FIVE SERIES.

Concentration.	Normal gelatin. $C_{H^+} = 1.5 \times 10^{-3}$		Iso-electric gelatin. $C_{H^+} = 2 \times 10^{-3}$		Gelatin chloride. $C_{H^+} = 3.1 \times 10^{-3}$		Made up in 0.0078N HCl.		Made up in 0.031N HCl.	
	$K$ .	$k_s$ .	$K$ .	$k_s$ .	$K$ .	$k_s$ .	$K$ .	$k_s$ .	$K$ .	$k_s$ .
2.00	....	....	....	....	10.10	10.34	....	....	....	....
2.50	....	....	....	....	10.52	10.64	....	....	....	....
3.00	....	....	....	....	10.06	10.96	....	....	....	....
3.50	....	....	....	....	10.85	10.96	....	....	7.88	8.70
4.00	....	....	7.18	7.98	10.72	10.94	8.06	8.79	8.20	8.92
4.50	7.95	8.46	7.88	8.55	10.57	10.89	8.38	9.00	8.70	9.26
5.00	8.62	8.97	8.41	8.93	10.47	10.91	8.78	9.26	8.74	9.26
6.00	9.57	9.57	8.76	9.03	10.27	10.96	8.86	9.12	8.86	9.12
7.00	9.16	9.36	8.92	8.92	9.64	10.51	8.92	8.92	8.92	8.92
8.00	8.92	9.36	8.56	8.75	9.32	10.44	8.75	8.99	8.68	8.90
9.00	8.48	9.11	8.18	8.55	8.82	10.14	8.42	8.87	8.42	8.87
10.00	8.13	8.97	7.88	8.46	8.40	9.94	8.66	9.63	8.00	8.63
11.00	7.71	8.73	7.57	8.37	7.97	9.72				
12.00	7.24	8.38	7.18	8.12	7.56	9.52				

In Figs. 1 and 2 the coefficient of viscosity,  $\eta/\eta_w$ , is plotted on the ordinate axis against the percentage of gelatin concentration on the abscissa

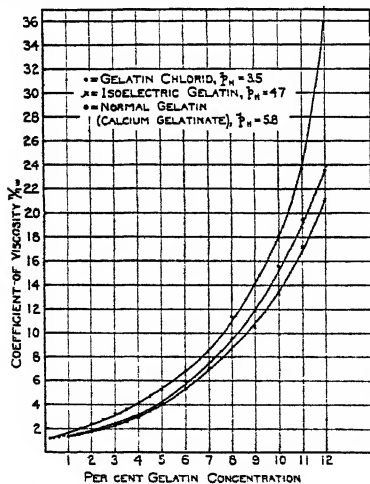


Fig. 1.—Relation of viscosity to concentration in gelatin solutions.

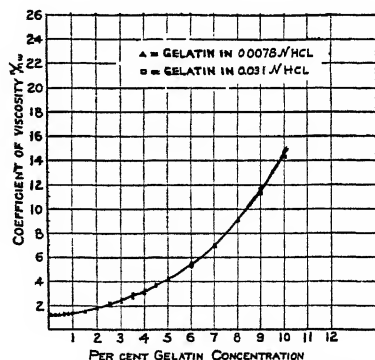


Fig. 2.—Relation of viscosity to concentration in gelatin solutions.

for the five series. In Fig. 3 the values of  $K$  are plotted against gelatin concentration.

### Discussion.

The data presented above reveal several points of interest, the most important being the failure to obtain a real constant for the ratio of  $A'/A$ . In each of the five series studied the value of this ratio rises to a maximum

with increasing concentration, and then as regularly, but more slowly, drops. Within a range of several per cent. the value of  $K$  varies but little, but the fact that, although the variation is small, it is nevertheless perfectly regular (except in special cases as noted below) can be interpreted in no other way than that a real constant is not obtained under the conditions of the experiment, and the variation may not be regarded as an experimental error.

In this connection it must be pointed out that in the calculations of Hatschek upon work reported by Botazzi and d'Errico on glycogen sols, and by Chick and Martin upon casein sols, the same regular rise to a maximum, in the value of  $K$ , followed by a similar regular drop, is observed. Hatschek makes no mention of this fact, however, and apparently regards the values attained as *constant* in the customary sense of the term. In Series I it will be observed that on carrying the concentration of the gelatin up to 30% the value of  $K$  had dropped from a maximum of 9.57 to 3.28. In experiments upon cellulose nitrate dissolved in 30% camphor-alcohol Sherrick<sup>9</sup> found similar results; *e. g.*, at a concentration of 2.54% his value for  $K$  was 34.64, and on increasing the concentration above that value the value of  $K$  also dropped as follows.

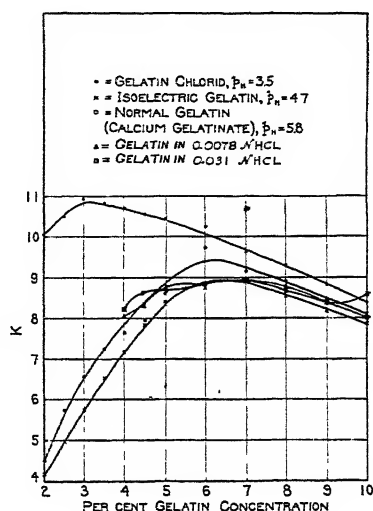


Fig. 3.—Variation in  $K$  with concentration of gelatin.

Concentration g. per 100 cc.	Absolute viscos- ity of sol.	Absolute viscos- ity of solvent.	A.	$A'$ .	$A'/A$ .	Percentage vol- ume of sol. occu- pied by solvated disperse phase.
2.54	23.03	0.96	1.1364	39.37	34.64	88.00
4.00	205.21	0.96	1.0142	25.00	24.65	98.6
7.50	565.65	0.96	1.0050	13.33	13.27	99.5
10.00	960.95	0.96	1.0030	10.00	9.97	99.7
12.00	1372.30	0.96	1.0020	8.33	8.31	99.8
15.00	3201.00	0.96	1.0010	6.666	6.66	99.9

The value of  $K$  may be analyzed as follows.

$$\frac{A'}{A} = \frac{\text{total volume}}{\text{dispersed weight}} \times \frac{\text{dispersed volume}}{\text{total volume}} = \frac{\text{dispersed volume}}{\text{dispersed weight}}$$

In other words  $K$  represents the volume occupied by unit weight of the dispersed phase. At low concentrations the structure upon which the formula is based is not present and accordingly the above statement

<sup>9</sup> J. L. Sherrick (Mellon Institute); personal communication.

may be applied only to more concentrated sols, but as soon as the necessary concentration is reached, it would be expected that the formula would accurately represent the result until such an amount of dispersed phase was present that there no longer was sufficient water, or other dispersing medium, present to allow the solvate action to proceed to its maximum. As soon as that concentration was reached the volume occupied by unit weight of dispersed phase ( $K$ ) would thereafter decrease with increasing concentration. But an examination of the data shows that the total volume of dispersed phase ( $K \times C$ ) has in no case except in the last experiment listed in Series 1 reached a value approaching the total volume of the system. Indeed, in the present experiment the maximum value of  $K$  is reached when the total volume of dispersed phase is only 32.8% of the total volume of the system in the case of the gelatin chloride, and 57.4 and 62.4% respectively in the other series. In the cases of the glycogen and casein sols previously mentioned the maximum value of  $K$  is obtained when the volumes of dispersed phase are 77.4 and 68.6% respectively of the volumes of the systems. In every case cited the value of  $K$  drops regularly from this point. Only in the experiments of Sherrick may this drop be explained as due to an actual insufficiency of dispersing medium for in his determinations the volume of dispersed phase is already 88.00% at the lowest concentration which he employed, and very quickly rises above 99%.

It is, therefore, pertinent to raise the question: Why does the volume occupied by unit weight of dispersed phase decrease with increasing concentration after attaining a definite maximum? (We are admitting the validity of Hatschek's postulations by which he formulated his equations, and therefore assume the value  $A'/A$  to express correctly the volume per unit weight of dispersed phase.) Two possible causes may bring about this decrease in volume; the increasing surface tension of the dispersion medium, or an actual reversal of phase. From a consideration of the laws of surface tension it becomes evident that as the number of particles of dispersed phase (the concentration) increases, the film of liquid separating them must become ever thinner and thinner in order to maintain its continuity. As this process continues the free surface of the dispersion medium becomes ever greater, and this may take place only at an expenditure of energy, *e. g.*, it is opposed by the surface tension of the liquid, and the greater the surface under stress, the greater will be the force opposing further increase in free surface. We may regard this force as entering into competition for the liquid against the solvate potential of the dispersed particles. An equilibrium must therefore be attained between these two forces at any given concentration.

Surface tension (of dispersion medium)  $\rightleftharpoons$  Solvation potential (of dispersed phase).

An excess of liquid will increase the solvation potential of the dis-



persed phase and an excess of dispersed particles will increase the surface energy of the dispersion medium.

The extent to which the surface tension may influence the solvation, and consequently the volume occupied by unit weight of dispersed phase, is shown to be a function of the percentage volume of the dispersion medium and if we may regard that volume of dispersion medium at which the dispersed phase reaches its maximum volume per unit weight as the point of neutrality in the above equation, the two forces there being equal, then the increasing effect of the surface tension is found to follow very nearly the empirical expression,

$$\sqrt[3]{V_m^0} - \sqrt[3]{V_m} = s, \quad (4)$$

where  $V_m^0$  is the volume of dispersion medium when  $A'/A$  is at its maximum,  $V_m$  is the volume of the dispersion medium at any other concentration, and  $s$  is the decrease in volume per unit weight of dispersed phase at the concentration  $V_m$ . Then

$$K \pm s = k_s, \quad (5)$$

where  $k_s$  is a constant corrected for surface tension.  $s$  is added at concentrations of dispersed phase greater than that at  $V_m^0$ , and subtracted at the lower concentrations. In Table I, Col. 6 shows the value of  $V_m$  and Col. 7 the value of  $k_s$ . The values of  $K$  and  $k_s$  for the five series are shown in Table II. In Fig. 4  $k_s$  is plotted against gelatin concentration.

In the case of the gelatin dissolved in 0.0078 *N* and in 0.031 *N* hydrochloric acid the uniform variations and consistency of direction which characterize the curves for the gelatin chloride, the iso-electric gelatin, and the calcium gelatinate, are not obtained. This is true for both the  $K$  and the  $k_s$  concentration curves. The reason for this difference in behavior of these two gelatins is not obvious, but it undoubtedly is connected with the presence of the free acid in the solution, and the variation, by the alteration in gelatin concentration, of the hydrogen-ion concentration of the system. Further study will be made of these special cases.

If the process of stretching out the thin film of dispersion medium by increasing concentration is continued beyond a certain point, this film

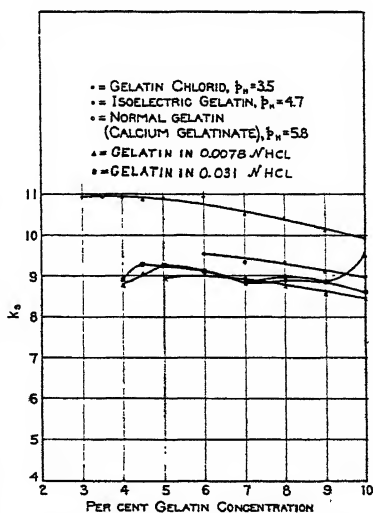


Fig. 4.—Variation in  $k_s$  with concentration of gelatin.

must break and cease to be continuous. When this happens there will probably follow a reversal of phase. The previously dispersed phase will become continuous, and the former dispersion medium will become dispersed. When this happens the formula of Hatschek would no longer hold good, as the system has suffered an abrupt change not accounted for in his equations. This fact might also explain the failure of Hatschek's  $K$  to remain constant, but it would scarcely be expected that a reversal of phase would occur at the low concentrations where the value of  $K$  begins to decline in gelatin sols.

Another point which is well brought out in the present work, and is made manifest by a comparison of the several columns in Table II, and by the curves in Fig. 1, is the wide variation in the viscosity of gelatin in different states of hydrogen-ion concentration, and in the volume occupied by unit weight of gelatin in these different states. As shown in Table II, the maximum volume per unit weight of gelatin chloride, at a hydrogen-ion concentration of  $3.1 \times 10^{-4}$  is 10.96, and is attained at a gelatin concentration of 3%, while in the case of iso-electric gelatin the maximum volume per unit weight is only 8.92 and is not reached until a concentration of 7% of gelatin is present. The untreated gelatin, which is calcium gelatinates of a hydrogen-ion concentration of  $1.5 \times 10^{-6}$ , attains a maximum of 9.57 at a concentration of 6%. It is especially interesting that in the case of the gelatin which is treated with acid, and the excess of acid *not* removed, the maximum volume reached, and the concentration of gelatin at that point, are identical with those of the iso-electric gelatin. In other words an excess of acid retards solvation in the sol state. That viscosity and solvation run parallel is evidenced by the fact that the higher the viscosity, the higher also is the value of  $K$ .

### Summary.

Experiments have been carried out upon gelatin sols to determine accurately the relation between viscosity and concentration. The data obtained have been applied to Hatschek's formula for the viscosity of emulsoids, and it is shown that the value  $A'/A$ , representing the volume occupied per unit weight of dispersed phase, is not a constant with varying concentration, but that this value rises regularly to a maximum, and thereafter regularly declines with increasing concentration. This behavior is noted also to exist in the cases of other colloids. A tentative explanation is presented based upon the effect which increasing concentrations of dispersed phase will have upon the surface tension of the dispersion medium. Assuming the equilibrium,

surface tension  $\rightleftharpoons$  solvation potential,

an empirical relation is developed which, with a fair degree of accuracy, defines the equilibrium. At very high concentrations a reversal of phase

probably occurs, at which point no expressions yet developed adequately represent the relations involved.

A high degree of solvation is shown to be indicated by a high coefficient of viscosity, *e. g.*, solvation and viscosity are parallel functions.

Iso-electric gelatin at a hydrogen-ion concentration of  $2 \times 10^{-5}$  is shown to have the lowest viscosity and the lowest degree of solvation, gelatin chloride at a hydrogen-ion concentration of  $3.1 \times 10^{-4}$  the highest, and calcium gelatinate at a hydrogen-ion concentration of  $2.5 \times 10^{-6}$  is intermediate.

If an excess of acid is allowed to remain in the gelatin solution, even though the acid be of very low concentration, the viscosity and degree of solvation will be retarded.<sup>10</sup>

PITTSBURGH, PA.

<sup>10</sup> In comment upon the above paper Dr. Emil Hatschek has written the author as follows.

"I think that my method of attack is correct in principle, but it involves several assumptions which go perhaps too far in the direction of simplifying the phenomena. One is obviously the assumption of spherical particles which, on crowding, become simple polyhedra. The gelatin molecule or aggregate is probably far from being of so simple a shape. If we had some information regarding it, the matter could probably be dealt with again, but, in the absence of such information it would be a fruitless mathematical exercise to investigate nonhomogeneous assemblages. That the formula applies, on the other hand, to deformable particles of a shape far different from the simple spherical, but still very symmetrical, is proved by the surprising closeness with which it fits red blood corpuscles. (E. Hatschek, *Kolloid Z.*, 27, 163 (1920).)

"The second point is the inconstancy of the degree of hydration or, generally, solvation. I had noticed this, in trying to fit the formula to rubber, etc., sols, but have not published anything in that respect. The simplest explanation seems to me this: the formula assumes that the continuous phase is *pure dispersion medium*, and that all the colloid is in the disperse phase, associated with some dispersion medium. Now this is probably also an undue simplification of the conditions. It is probable that the dispersion medium also contains some of the colloid, and it seems to me at least possible that the proportion may change, *i. e.*, the ratio, colloid in disperse phase: colloid in continuous phase, may become smaller with increasing concentration.

Both suggestions you make are very interesting. The interfacial tension between the two phases, being due only to the difference in concentration, can be very small only, but that would not prevent its defining an equilibrium. The suggestion that a reversal of phases may take place is ingenious, but one would like to have some further evidence to support it. It seems to me it would almost certainly entail a break in the viscosity-concentration curve, of which there is no indication. There is also the possibility that the hydration may really decrease at higher concentration, as it does with some true solutes. I think a clue to the distribution of water may perhaps be afforded by the solubility of gases, or liquids like ether, in gelatin sols—but the results published so far, particularly by A. Findlay, seem very difficult of interpretation."

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## AN ATTEMPT TO PREPARE NITRO-NITROGEN TRICHLORIDE. II. THE CONDUCT OF MIXTURES OF NITROGEN AND CHLORINE IN A FLAMING ARC.

BY WILLIAM ALBERT NOYES.

Received April 11, 1921.

Eight years ago<sup>1</sup> an account was given of experiments designed in the hope of preparing a nitro-nitrogen trichloride in which the chlorine atoms would be negative and which would hydrolyze normally to hydrochloric and nitrous acids in contrast with the ordinary nitrogen trichloride in which the chlorine atoms are positive and show a tendency always to separate in such a manner as to be replaced by hydrogen, while the chlorine atoms have twice the oxidizing power of the atoms of free chlorine.<sup>2</sup>

Since that article was published evidence for the composite nature of chemical atoms has accumulated rapidly and chemists seem ready to accept the view that atoms are composed of electrons and positive nuclei held together by either static or dynamic electrical forces or by a combination of the two. The distinction between nuclear electrons, which remain unchanged in their relation to the nucleus of the atom, and valence electrons, which take part in some manner in reactions between atoms, seems also to be universally accepted by those who discuss questions of this character at all.

Three more or less distinct hypotheses have been proposed to account for the mechanism by which valence electrons hold atoms in combination.

1. J. J. Thompson,<sup>3</sup> who was the first to state the concept of valence electrons clearly, proposed the hypothesis that atoms consist of a sphere of positive material with electrons inside and valence electrons transferred completely from one atom to the other in chemical combination. Nearly all of the purely chemical discussion by Falk and Nelson, Fry, Jones, Stieglitz and others has made use of this simple notion of the transfer of electrons.

2. Ramsay<sup>4</sup> suggested that an electron might serve as a connecting link between atoms. In almost or quite the last paper that he published<sup>5</sup> he described an apparatus designed to show that atoms may be held in combination by the magnetic attraction between rotating electrons. Bohr<sup>6</sup> also supposed that atoms may be held in combination by elec-

<sup>1</sup> THIS JOURNAL, 35, 767 (1913).

<sup>2</sup> For recent evidence for this point of view see *ibid.*, 42, 2167 and 2173 (1920).

<sup>3</sup> J. J. Thompson, *Phil. Mag.*, 7, 237 (1904).

<sup>4</sup> Ramsay, *J. Chem. Soc.*, 93, 774 (1908).

<sup>5</sup> Ramsay, *Proc. Roy. Soc.*, 92A, 451 (1916).

<sup>6</sup> Bohr, *Phil. Mag.*, 26, 1, 476, 857 (1913).

trons rotating about the line joining the centers of the atoms, the attraction being static rather than magnetic. Parson<sup>7</sup> has also developed an elaborate magneton theory

3. G. N. Lewis,<sup>8</sup> in an hypothesis which has been elaborated and brought to the attention of a wide circle of chemists by Irving Langmuir,<sup>9</sup> makes the following suppositions.

(a) Every atom has a central kernel composed of positive units and electrons, the latter being, of course, the nuclear electrons referred to above. X-rays seem to be emitted from these nuclear electrons.

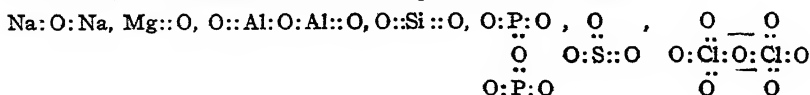
(b) The central kernel is identical with the atom and has a zero charge for elements of the zero group. It has a unit positive charge for hydrogen and an excess of positive charges varying (by whole units) from 1 to 7 for other atoms. The words in parenthesis are not included in the statement of Professor Lewis but seem to be justified by the experimental evidence.

(c) Neutral atoms have an outer shell of electrons varying from 1 to 8. The positive charge of the kernel is exactly balanced by the negative charges of these electrons.

At the April meeting of the National Academy of Sciences, R. A. Millikan gave evidence from the spectrum lines beyond the ultra-violet which affords very strong support for this part of the hypothesis and which seems to prove that these electrons of the outer shell are very far from the center of the atom in comparison with the nuclear electrons which emit X-rays. It seems evident that the electrons of the outer shell are the valence electrons.

(d) Atoms may give up electrons from the outer shell, forming positive ions, or take electrons from other atoms, forming negative ions, 7 or two atoms may hold 2 (or 4) electrons in common forming "non-polar" compounds.

(e) It seems to follow from the hypothesis as stated that no atom can be in direct union with more than 4 other atoms. It is at this point that the hypothesis differs most radically from theories of valence previously current. It does not seem to agree very well with the existence of such compounds as  $\text{PCl}_5$ ,  $\text{SF}_6$ ,  $\text{S}(\text{OH})_6$ , etc., though Langmuir has attempted an explanation of some of these.<sup>10</sup> It does not give a very satisfactory picture of the apparent regular increase of valence from 1 to 7 in the series of oxides  $\text{Na}_2\text{O}$ — $\text{Cl}_2\text{O}_7$  and in the corresponding acids. According to the hypothesis of Lewis this series of oxides is represented as follows:



An examination of these formulas makes it clear that in phosphorus pentoxide and in sulfur trioxide two of the double unions of the older formulas have become single unions while in chlorine heptoxide three double unions have become single unions.

The hypotheses of Bohr and of Lewis agree with the evidence of the scattering of  $\alpha$ -particles by thin films presented by Rutherford.<sup>11</sup> He

<sup>7</sup> Parson "A Magneton Theory of the Structure of the Atom," *Smithsonian Inst. Pub.*, 65, No. 11 (1915).

<sup>8</sup> Lewis, *THIS JOURNAL*, 38, 762 (1916).

<sup>9</sup> Langmuir, *ibid.*, 41, 868 (1919).

<sup>10</sup> I understand that Lewis assumes a higher value than 4 in some cases but I do not know that such a statement has been published.

<sup>11</sup> Rutherford, *Phil. Mag.*, 21, 669 (1911).

considers that this evidence has demonstrated that the positive nuclei of atoms have a volume very small in comparison with the effective size of the atoms. J. J. Thompson's hypothesis of a sphere of positive material with embedded electrons has, therefore, been abandoned. The question whether there is a transfer of an electron from one atom to another in all forms of chemical combination or whether this occurs only in the so-called "polar" compounds, and the question whether atoms are held together by a single electron or by pairs of electrons may well be considered as still open.

Nitrosyl chloride,  $\text{NOCl}$ , hydrolyzes to nitrous and hydrochloric acids. According to the hypothesis of Professor Lewis, the two electrons which hold the atoms of nitrogen and chlorine together remain with the chlorine atom in the decomposition of the nitrosyl chloride, but they remain with the nitrogen atom in the decomposition of nitrogen trichloride, or of chloroamine,  $\text{NH}_2\text{Cl}$ . The difference in conduct may be explained as due to the oxygen atom in the nitrosyl chloride but, if it were possible to prepare an isomeric nitrogen chloride in which the chlorine would tend to separate as a chloride ion, the hypothesis that there is a pair of electrons between the atoms would become far less probable. The question seems one of sufficient theoretical importance to justify the considerable amount of time which has been spent on the experiments described in this paper.

Nitrogen and oxygen combine at a very high temperature to form the endothermic compound, nitric oxide, in which the nitrogen is usually assumed to be positive and the oxygen negative. It seemed possible that a nitrogen dichloride in which the chlorine would be negative might be formed in a similar manner. So far as the writer is aware no one had ever tried the experiment. The first experiments, in which an ordinary induction coil and heavy platinum wires were used, were begun about 7 years ago and the study of the problem has been continued at intervals up to the present. The final result of the investigation is negative and it is unnecessary to describe in detail a dozen or more different modifications of the apparatus used.

The two forms which were longest used and which seem to be best adapted for such a purpose are shown in the figures.

The air was displaced by nitrogen passed in from the top and liquid chlorine was condensed in the small bulb at the bottom. The apparatus was then closed and a circulation of the nitrogen mixed with chlorine, at the vapor pressure of liquid chlorine at the temperature of carbon-dioxide snow mixed with alcohol, was produced by the heat from the discharge in the bulb and by cooling the side tube with ice. The electrodes were attacked by the chlorine and it was never possible to continue the experiments more than a few hours before they were perforated. In a considerable number of experiments the periods of operation were from 1 to 3 hours

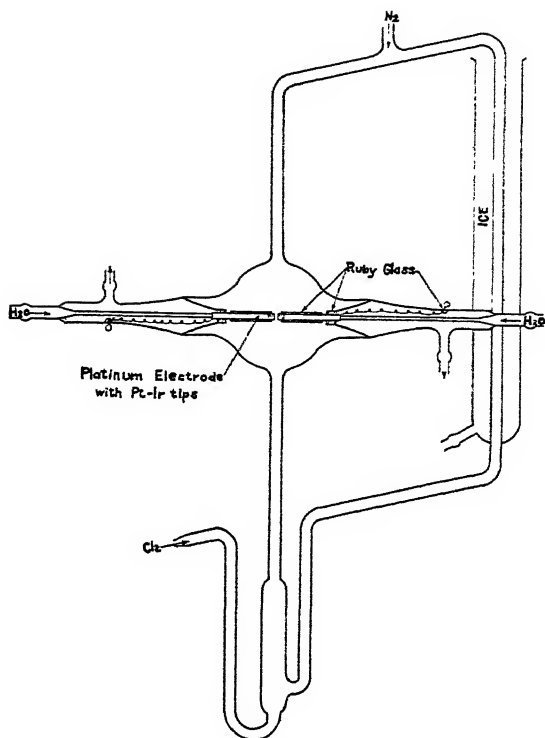


Fig. 1.

Fig. 1 shows a bulb with a capacity of about 350 cc. Two hollow platinum electrodes with heavy platinum-iridium tips were used. Between these electrodes an alternating discharge was produced by a Thorardson transformer rated at 110/10,000 volts. The electric flame was spread to an area of 4 to 5 sq. cm. by a very powerful electro-magnet having the poles properly placed on the two sides of the bulb.

and in two experiments for 8 and 10 hours respectively. At the close of the run the chlorine was allowed to evaporate and pass through water to hydrolyze the product and the gases remaining in the apparatus were driven through the water by nitrogen or air. The nitric acid formed in this way was determined by reduction to ammonia.

Careful blank tests for compounds of nitrogen were run on the mixture of the two gases placed in the tube in the usual manner, as well as on the water used for hydrolysis, with absolutely negative results. The first four runs with this apparatus lasting from 1 to 4 hours have values for combined nitrogen ranging from 0.5–1.0 mg. The next two of 3.5 and 2 hours duration gave 0.2 and 0.3 mg; while in the seventh run lasting 8 hours, analysis indicated only 0.07 mg. From the well-known difficulty in removing moisture from glass it seems probable that the yields

were due to interaction between nitrogen in the arc with either oxygen or hydrogen from decomposed moisture. With the gradual elimination of this absorbed water the yields decreased. In the eighth run 2 or 3 drops of water were added to the chlorine forming a small visible lump of ice. The vapor pressure of the ice is small at the temperatures used, below  $0^{\circ}$ , so that but little escaped, and during a 10-hour run only 0.17 mg. of nitrogen was brought into combination.

In the endeavor to "freeze out" any compound of nitrogen and chlorine that might be formed, an apparatus was made where the arc, spread as before, was allowed to strike between platinum-iridium electrodes close to the surface of liquid chlorine in an atmosphere of chlorine and pure nitrogen.

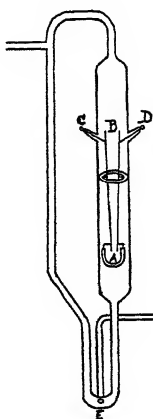


Fig. 2.

A quartz tube protected the glass walls from the heat of the arc. Four completed runs were made lasting from 1 to 2.5 hours with the formation of no appreciable amount of nitrogen compound. Other forms of apparatus designed to bring the gases after leaving the arc more quickly into contact with a cooled surface gave negative results with a spread arc. A silent discharge likewise gave negative results.

The last form of apparatus to be used, and the most satisfactory, is shown in Fig. 2.

Two platinum wires, A B, 18 cm. long and 0.5 mm. in diameter, but made heavier at the top by putting 3 or 4 pieces of the wire together, were supported from the platinum connections C and D and held in place by the circular rod of Pyrex glass bearing platinum wires welded to the longer wires and by a U-shaped rod of Pyrex glass at the bottom.

By this arrangement contact of the electric flame with the glass supports was completely avoided. The wires were placed about 4 mm. apart at the bottom and 15 mm. apart at the top. These distances were fixed by careful preliminary experiments. The distance at the bottom must be such that a discharge from the Thorardson transformer will pass between the wires and immediately begin to travel up the wires as the gases above the discharge become heated. If the distance is too great the discharge will not pass and if too small it remains at the bottom and soon melts the ends of the wires. The distance at the top is such that when the discharge reaches that point a flaming arc is produced. In a part of the experiments (1-10) recorded in the table (p. 1780), wires 50 cm. long, 4 mm. apart at the bottom and 20 mm. apart at the top, were used. With this form of apparatus the arc would break when it reached the top, and start again at the bottom. This was more difficult to regulate than the stationary arc. Dr. Rideal suggested this form of apparatus and we understand that it has been used in commercial practices.



The nitrogen was prepared by passing a mixture of air and purified hydrogen, from a Kipp generator, through a hard glass tube about 80 cm. in length placed in a combustion furnace. The tube was filled at first with copper oxide, and about half of this was reduced to metallic copper. It is easy to regulate the rates for the hydrogen and air so that the relative amounts of copper and copper oxide remain nearly constant; and if these are moderately hot it is impossible for either oxygen or hydrogen to pass beyond the tube. The nitrogen was dried with conc. sulfuric acid and phosphorus pentoxide. Chlorine was prepared by warming a mixture of sodium dichromate and hydrochloric acid and was condensed in a bulb surrounded by carbon-dioxide snow and alcohol and introduced through a side tube sealed to the tubes between the sulfuric acid bottle and the phosphorus pentoxide tube.

All parts of the apparatus were sealed together. In the last experiment where the negative result was most conclusive, a current of nitrogen was passed through the apparatus at first for 5 hours and it was then surrounded with asbestos and heated from below to 100° or 130° while the current of nitrogen was continued and the arc maintained for 18 hours longer. The chlorine was then introduced and condensed in the lower bend of the apparatus by surrounding this with carbon-dioxide snow and alcohol. Nitrogen was again passed through the apparatus for some time and the arc was operated for 51 hours. The upright tube at the left side of the apparatus was about one cm. in diameter, and during the operation of the arc the circulation of the gases through the system was sufficiently rapid so that the tube on the right through which the cold gases rose into the larger tube became covered with frost.

At the close of the experiment the carbon dioxide snow was removed and the chlorine was allowed to evaporate and pass through the hydrolysis tube shown in Fig. 3. The spiral tube is 185 cm. in length and only 2 mm. in diameter. If 2 or 3 cc. of water is placed in the apparatus, gas entering at A pushes short columns of water around the spiral to B, from which point the water is returned through the upright tube to C. This secures a very effective contact between the gas and liquid with the use of a very small amount of water.

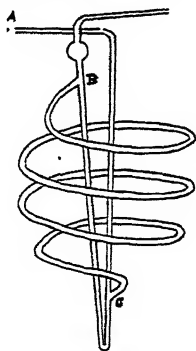


Fig. 3.

If any nitro chloride of nitrogen were formed it would be converted to nitric acid by the chlorine passing the hydrolysis apparatus with it.  $\text{NCl}_3 + \text{Cl}_2 + 3\text{H}_2\text{O} = \text{HNO}_3 + 5\text{HCl}$ , or  $2\text{NCl}_2 + 3\text{Cl}_2 + 6\text{H}_2\text{O} = 2\text{HNO}_3 + 10\text{HCl}$ . The ratio of nitrogen to chlorine, irrespective of the composition of the nitrogen chloride, would be 1:5. It was shown that pure chlorine left only the merest trace of combined chlorine in the water when it was passed through the spiral and followed by nitrogen or air.

If nitrosyl chloride were formed in the apparatus because of the pres-

ence of a trace of oxygen or of moisture the ratio of nitrogen to chlorine would be 1:3:  $\text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O} = \text{HNO}_3 + 3\text{HCl}$ .

If the vapor of ordinary, ammonio-nitrogen trichloride is passed through the spiral tube it was demonstrated that practically no hydrolysis occurs. On the other hand, if the vapor is passed through conc. hydrochloric acid, ammonium chloride and chlorine<sup>12</sup> are formed. The products formed in the arc were tested in that way with negative results.

After the completion of an experiment the water in which the products were hydrolyzed was diluted to a standard volume and the combined nitrogen and chlorine were determined in aliquot portions. The nitrogen was determined by reduction in an alkaline solution with Devarda's alloy, and the chlorine by precipitation with silver nitrate. The results of 13 experiments were as follows.

Expt.	No. of hours arc was operated.	Mg. atoms. N.	Mg. atoms. Cl.
1	10	1.54	4.20
2	20	0.11	0.113
3	18	0.96	2.96
4	20	0.44	1.05
5	30	0.66	2.80
6	14	0.12	0.35
7	10	0.20	0.60
8	10	0.05	0.18
9	6	0.02	0.05
10	8	0.01	0.07
11	38	0.06	0.22
12	53	0.05	0.57
13	51	0.006	0.024

In the earlier experiments, in which the extreme care of the later experiments to remove traces of oxygen and moisture was not observed, appreciable amounts of combined nitrogen were formed, but the ratio of nitrogen to chlorine was much less than 1:5 and in those cases where most nitrogen was formed approximated 1:3. It seems quite certain that the compound present in these cases was nitrosyl chloride. The evidence of the later experiments seems practically conclusive as demonstrating that if nitrogen and chlorine combine at all in the flaming arc the compound is decomposed as it escapes from the zone of heat.

In all of the experiments with platinum electrodes a grayish-brown deposit was formed on the walls of the tube. Expts. 6 to 10 of the table were carried out consecutively. The solution obtained by washing the apparatus out with water, contained 0.75 mg. atoms of combined nitrogen. The wash solutions from Expts. 11 and 12 contained 0.33 mg. atom, while that from the last experiment contained only 0.02 mg. atom of combined nitrogen.

<sup>12</sup> Noyes, *THIS JOURNAL*, 42, 2173 (1920).

The ratio of platinum to chlorine was also determined in the solutions. In the last experiment the atomic ratio was 1:3.6, indicating a mixture of platinic chloride,  $\text{PtCl}_4$ , with a little platinous chloride. In two earlier experiments the atomic ratios were 1:5.76 and 1:5, indicating the presence of chloroplatinic acid. The hydrochloric acid to form this probably came from the interaction of moisture, chlorine and nitrogen:  $\text{N}_2 + 2\text{Cl}_2 + 2\text{H}_2\text{O} = 2\text{NOCl} + 2\text{HCl}$ .

Several experiments were tried with carbon electrodes. The results were similar, but appreciable amounts of a white solid and of a colorless liquid were formed, doubtless carbon hexachloride and carbon tetrachloride.

To test the efficiency of the apparatus a run was made with air passing through it at the rate of 3.6 liters per hour. The oxides of nitrogen condensed almost completely in the lower part surrounded by carbon-dioxide snow and alcohol, as colorless crystals of nitrogen tetroxide, with only a little blue nitrous anhydride. About 30 mg. atoms of combined nitrogen were obtained in 2 hours—250,000 times as much as was obtained in the same time in the last experiment with nitrogen and chlorine.

Experiments were also tried with a very efficient ozonizer of Pyrex glass, consisting of two concentric tubes 55 to 60 cm. long and 2.8 and 3.7 cm. in diameter, respectively. The inner tube was filled with a solution of sodium sulfate and the outer tube was surrounded with the same electrolyte. A copper spiral running to the bottom of the inner tube and another wound around the larger tube furnished the connection with the terminals of the Thorardson transformer. When the latter was connected with the 110 volt circuit, quantities of ozone were produced in air passed between the tubes but no combined nitrogen was found. With 220 volts there was a crackling sound with a blue glow, and a large number of streamers appeared between the walls of the tubes. Under these conditions air passed through the apparatus gave 0.15 mg. of combined nitrogen in 30 minutes but a mixture of nitrogen and chlorine passed for 6 hours gave no combined nitrogen. A negative result was also obtained with the conditions which gave ozone but no combined nitrogen.

When active nitrogen prepared by Strutt's method was passed over chlorine at the temperature of liquid air no combination occurred.

### Summary.

1. It has not been found possible to prepare either a nitro-nitrogen chloride or ordinary nitrogen trichloride by passing a mixture of nitrogen and chlorine through a flaming electric arc.

2. So far as negative results have value, the experiments favor Professor Lewis's hypothesis that electrons are held jointly by two atoms

rather than the view that electrons are transferred from one atom to the other when atoms combine.

I wish to express my appreciation of the valuable assistance of L. C. Johnson, B. R. Honovski, F. O. Anderegg, A. B. Haw, and G. H. Coleman in carrying out the experiments described in this paper.

URBANA, ILL.

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[CONTRIBUTION FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY.]

## VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF NITRIC ACID.

BY WILLIAM C. SPROESSER AND GUY B. TAYLOR.

Received April 14, 1921.

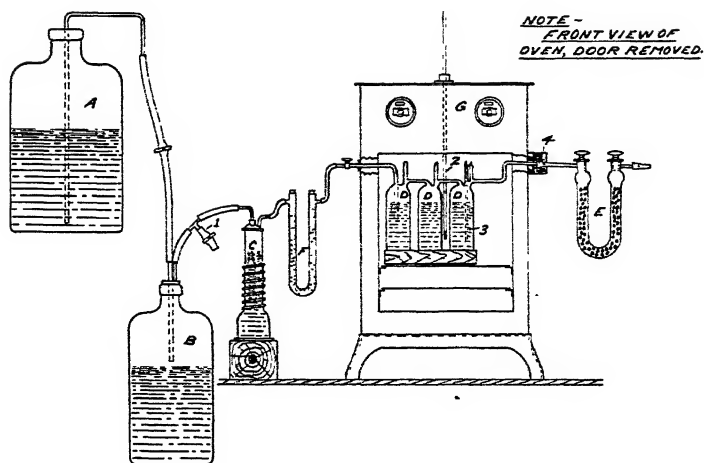
The partial pressures of water and nitric acid vapors in equilibrium with all concentrations of aqueous nitric acid possess scientific interest and are practically useful to the acid industry. Burdick and Freed<sup>1</sup> have recently supplied data for concentrations ranging from 24% to 70% nitric acid at 25°, 50°, and 75°. The present investigation had as its object the extension of similar data to 100% nitric acid and over a wider temperature range. The dynamic method chosen did not prove suitable for concentrations above 80%, owing to thermal decomposition of nitric acid vapor. The measurements covered the range from 20 to 90% at temperatures from 0° to 80° and, therefore, considerably extend the range, making it possible to draw a series of curves showing the acid composition of minimum vapor pressure within these temperature limits.

### Experimental.

The apparatus is shown in Fig. 1. Water from the reservoir A was siphoned into the calibrated bottle B, displacing a known volume<sup>2</sup> of air and forcing it through the dryer C, the carbon dioxide-remover F, the three saturators D, and the absorbers E. The dryer C was a Friedrichs "spiral" gas-wash-bottle containing conc. sulfuric acid. The U-tube F was filled with soda lime. The saturators D were special forms of spiral wash-bottles. In the last bottle a small accurate Anschütz thermometer, 3, was sealed to record the temperature, which was maintained constant to  $\pm 0.1^\circ$ . The three saturators were filled with nitric acid of known composition, fused together, and placed in the Freas constant-temperature oven G. The ground-glass joint, 4, connected the absorbers E to the rest of the system. The whole apparatus was always set up so that nitric acid, liquid and vapor, came in contact with glass only. To avoid condensation in the tube and ground joint protruding from the oven, an electrically heated wire-spiral was placed about the ground joint, 4, to keep the joint warm. The U-tube E, filled with solid sodium hydroxide and followed by two or more such tubes (not shown) containing as well, layers of phosphorus pentoxide on glass wool, was used to absorb the effluent vapors.

<sup>1</sup> Burdick and Freed, *THIS JOURNAL*, 43, 518 (1921).

<sup>2</sup> Calculated from the volume of the bottle, temperature and pressure within the bottle, and the barometric pressure.



ARRANGEMENT OF APPARATUS USED TO DETERMINE  
VAPOR PRESSURES OF NITRIC ACID SOLUTIONS.

After ascertaining the gain in weight of the U-tubes, the nitric acid absorbed by the alkali was determined by the Devarda method and nitrite was estimated by permanganate when found to be present. The results at temperatures from  $35^{\circ}$  to  $82^{\circ}$ , were obtained with this apparatus.

The method used for measurements at  $0^{\circ}$  was somewhat different from that described above. Air was purified from carbon dioxide and dried by passing in succession through a caustic solution and conc. sulfuric acid. The purified air was then bubbled through the saturators, which were entirely immersed in ice-water. Leaving the saturators, the air was passed in succession through (1) a Vanier bulb containing a known amount of standard caustic solution, (2) a large U-tube containing stick sodium hydroxide, at the exit end of which were several layers of phosphorus pentoxide on glass wool, and finally (3) a gas meter accurate to 0.001 cu. ft. The experiments were conducted in a constant-temperature room in order to determine accurately the volume of air passed through the saturators. At the exit end of the saturators there was a pressure of about 10 mm. mercury (above atmospheric) and in the vapor-pressure calculations a correction was made for this added pressure.

Equilibrium was assured at all temperatures by the usual expedient of varying the rate of air flow. Much faster rates than those used in any of the final experiments gave the same results.

TABLE I.  
 SUMMARY OF EXPERIMENTAL RESULTS.

Nitric acid. %,	Temp., °C.	Composition of vapor,			Calculated vapor pressures (mm. Hg).			
		%HNO <sub>3</sub> .	%H <sub>2</sub> O.	%NO <sub>2</sub> .	Total.	HNO <sub>3</sub> .	Partial. H <sub>2</sub> O.	NO <sub>2</sub> .
21.25	0.0	0.00	100.00	....	3.8	...	3.8	...
20.65	35.0	0.21	99.79	....	36.8	...	36.8	...
20.65	50.0	0.13	99.87	....	79.9	...	79.9	...
20.65	65.0	0.19	99.81	....	155.6	0.1	155.5	...
20.65	80.0	0.42	99.58	....	293.9	0.4	293.9	...
40.82	0.0	2.02	97.98	....	2.5	...	2.5	...
40.03	35.1	4.38	95.62	....	26.1	0.3	25.8	...
40.03	50.0	3.81	96.19	....	55.6	0.6	55.0	...
40.03	65.0	5.11	94.89	....	117.6	1.8	115.8	...
40.03	80.0	6.40	93.60	....	224.2	4.2	220.0	...
56.26	0.0	22.49	77.51	....	1.4	0.1	1.3	...
56.16	35.0	33.12	66.88	....	17.0	2.1	14.9	...
56.16	50.0	33.87	66.13	....	39.4	5.0	34.4	...
56.16	64.9	33.69	66.31	....	84.6	10.6	74.0	...
56.16	82.0	34.39	65.61	....	182.5	23.5	159.0	...
68.64	0.0	81.03	18.97	....	1.1	0.6	0.5	...
68.42	35.3	69.15	30.85	....	15.9	6.2	9.7	...
68.42	50.1	69.06	30.94	....	35.7	13.7	22.0	...
68.42	74.0	68.76	31.24	....	118.3	45.6	72.6	...
68.42	80.1	68.32	31.68	....	152.8	58.2	94.6	...
79.07	0.0	94.87	5.13	....	2.7	2.4	0.3	...
80.23	35.0	88.56	11.44	....	22.1	15.2	6.9	...
80.23	52.0	89.03	10.92	0.05	50.3	35.2	15.1	...
80.23	65.0	88.49	11.43	0.08	90.0	61.9	28.0	0.1
80.23	82.1	87.13	12.88	0.49	195.2	129.3	65.0	0.9
88.24	0.0	97.75	1.06	1.19	7.8	7.3	0.3	0.2
90.63	35.8	98.27	1.62	0.11	69.7	65.9	3.7	0.1
90.63	50.0	96.55	2.40	1.05	136.2	123.6	10.7	1.9

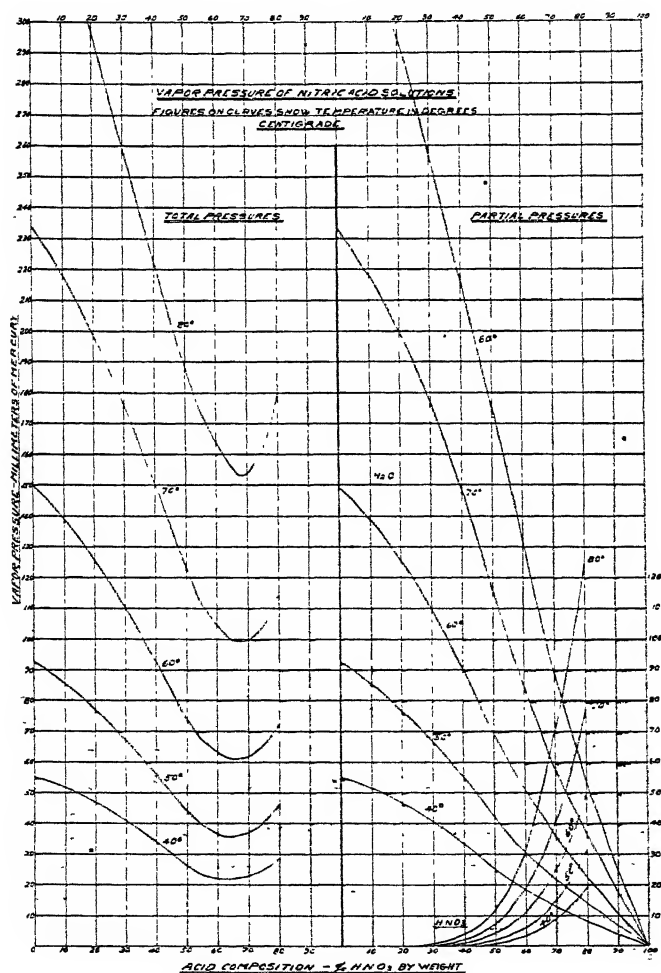
### Discussion of Results.

Table I summarizes the experimental results, giving averages of duplicate runs. The vapor pressures were calculated from the data in the usual manner, *i. e.*, the volume of air and weights of water and nitric acid were calculated to volumes under standard conditions, from which mol fractions were derived. Mol fraction multiplied by the measured pressure prevailing over the solution in the last saturator bottle gave the respective partial pressures. This method of calculation assumes that both water and nitric acid vapors follow the laws of perfect gases.

The experimental results given in Table I were plotted on a large scale to give the usual pressure-temperature curves. Curves were drawn for each acid composition and for the total and partial pressures. These curves were then carefully smoothed out so as to be consistent. From these smoothed curves the plot, Fig. 2, was constructed. On the original large scale plot, 1 mm. =  $\frac{1}{20}$  inch. The smoothed values

read graphically from this large scale plot are assembled in Table II, where the results are recorded to the nearest half millimeter,—no further significant figures being warranted by the precision of the experimental data and methods of calculation. The values in Table II and Fig. 2 are satisfactory for all technical calculations involved in acid manufacture.

Other measurements of the vapor pressures of nitric acid solutions have been made by Saposhnikoff,<sup>3</sup> Burdick and Freed,<sup>4</sup> and Creighton and Githens.<sup>5</sup> Saposhnikoff made his measurements at 15° on concen-



<sup>3</sup> Saposhnikoff, *Z. physik. Chem.*, 53, 225 (1905).

<sup>4</sup> Burdick and Freed, *THIS JOURNAL*, 43, 518 (1921).

<sup>5</sup> Creighton and Githens, *J. Franklin Inst.*, 179, 161 (1915).

trations of nitric acid ranging from 65 to 100%. Decomposition of nitric acid vapor into nitrogen oxides was encountered at the higher concentrations. Saposhnikoff used a dynamic experimental method and fails to give the method of computation of his results.

TABLE II.  
VAPOR PRESSURES OF NITRIC ACID SOLUTIONS.

Composition of solution. % $\text{HNO}_3$ by weight.	Pressure in Millimeters of Mercury.								
	Total pressures.								
	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.	80°.
0	4.5	9.0	17.5	31.5	55	92	149.5	234	..
10	4.0	8.0	16.5	30.5	52	86	139	219	..
20	3.5	7.5	15.5	29.0	47	77	126	199	295
30	3.0	7.0	14.0	25.5	41	67	110	176	259
40	2.5	6.5	12.5	21.0	34	55.5	92	151	222
50	2.0	5.5	10.5	16.5	25.5	44	73.5	124	188
60	1.5	4.0	8.0	13.0	22	36.5	63	104	164
70	1.0	3.5	8.0	12.5	22.5	37	61.5	99.5	153.
80	3.0	6.0	10.5	17.0	28.5	46	72	114	179
	Partial pressures of water vapor.								
0	4.5	9.0	17.5	31.5	55	92	149.5	234	
10	4.0	8.0	16.5	30.5	52	86	139	219	
20	3.5	7.5	15.5	29.0	47	77	126	199	295
30	3.0	7.0	14.0	25.5	41	67	110	176	258
40	2.5	6.5	12.5	21.0	33.5	55	91	149	217
50	2.0	5.5	10.5	16.5	25	42	69	117	176
60	1.5	4.0	8.0	11.5	18.5	31	51	85	132
70	0.5	2.0	4.5	6.5	13	21.5	36	58	89.5
80	0.5	1.5	2.5	4.5	8.5	14	23	37	54
	Partial pressures of nitric acid vapor.								
0	...	...	...	...	...	...	...	...	...
10	...	...	...	...	...	...	...	...	...
20	...	...	...	...	...	...	...	...	...
30	...	...	...	...	...	...	...	...	1.0
40	...	...	...	...	...	0.5	1.0	2.0	5.0
50	...	...	...	...	0.5	2.0	4.5	7.0	12.0
60	...	...	...	1.5	3.5	5.5	12.0	19.0	32.0
70	0.5	1.5	3.5	6.0	9.5	15.5	25.5	41.5	64.0
80	2.5	4.5	8.0	12.5	20.0	32.0	49.0	77.0	125.0

Burdick and Freed's measurements were also made by the dynamic method, and cover the range 24 to 70% acid at three temperatures, 25°, 50°, and 75°. Their results agree very well with those disclosed in this article. Below are compared the data of the two investigations for acid concentrations employed by both and at 50°.

% $\text{HNO}_3$ (S.-T.) (B.-F.)		Partial Pressure $\text{H}_2\text{O}$ (S.-T.) (B.-F.)		Partial Pressure $\text{HNO}_3$ (S.-T.) (B.-F.)		Total Pressure (S.-T.) (B.-F.)	
40.03	40.2	55.0	53.6	0.6	0.75	55.6	54.3
68.42	69.9	22.0	17.7	13.7	16.6	35.7	34.3



Creighton and Githens measured total vapor pressures by a static method. They determined the boiling temperatures under reduced pressures down to 75°. Their results are considerably higher than ours at corresponding temperatures and concentrations.

Kaltenbach<sup>6</sup> gives graphically the boiling points of nitric acid solutions at atmospheric pressure and the composition of the vapors in equilibrium with the boiling solutions. His results for the partial pressures of nitric acid vapor appear to be lower for concentrations below the acid of maximum boiling point and higher for those above than extrapolation of our results would indicate.

### Summary.

1. The total and partial vapor pressures of nitric acid solutions of concentrations approximately 20, 40, 56, 68, and 80% by weight at temperatures of 0°, 35°, 50°, 65°, and 80° have been measured.

2. From these data vapor pressures for each 10% increase in concentration and 10° rise in temperature have been calculated by graphic methods.

3. Attempts to measure the vapor pressure of 90% nitric acid were unsuccessful owing to decomposition of the acid at all the experimental temperatures except at 0°.

The authors wish to acknowledge the helpful advice of Mr. Roger Williams during the course of the investigation and the assistance of Mr. F. C. Blake in constructing the curves.

HENRY CLAY, DELAWARE.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## A HIGH PRESSURE DUE TO ADSORPTION, AND THE DENSITY AND VOLUME RELATIONS OF CHARCOAL.<sup>1</sup>

(Papers on Surface Energy and Surface Forces.)

BY WILLIAM D. HARKINS AND D. T. EWING.

Received May 2, 1921.

### 1. The Compression of Liquids by Charcoal.

While working on Problem 108 of the National Research Council in the year 1918 the writers discovered an interesting relationship, which is that the volume of different liquids adsorbed by the same charcoal

<sup>6</sup> Kaltenbach, *Chimie Ind.*, 2, 143 (1919).

<sup>1</sup> Presented at the Philadelphia meeting of the American Chemical Society, September 1919. This problem was suggested to the National Research Council by the senior author. The data for one charcoal with 11 liquids were published in February 1920 (Harkins and Ewing, *Proc. Nat. Acad. Sciences*, 6, 49-56 (1920)). The present paper is an abstract of a thesis presented to the University of Chicago in August 1919 by D. T. Ewing, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

increases in the same order as the percentage compression for a definite high pressure,—such as twelve thousand atmospheres. Thus the charcoal seems to produce the same change in the volumes of liquids which penetrate it, as is given by a high pressure. In our preliminary report it was stated that while accurate calculations of the pressures which would have to be put upon these liquids to give the same percentage compressions, could not be made in the absence of data on an incompressible or very slightly compressible liquid, it seemed likely that the order of magnitude might be represented by twenty thousand atmospheres<sup>2</sup> in excess of the internal pressure of the liquid. While there is nothing novel in the idea of the existence of such powerful adhesional forces at the surface of a solid, their experimental demonstration in such a direct way is somewhat remarkable, since the highest values for the internal pressures of liquids thus far experimentally demonstrated<sup>3</sup> are 34 atmospheres with water at 24.4°, 39.5 atmospheres for ethyl alcohol at 22.5°, and 72 atmospheres for ether at 17.7°.

Our hypothesis that the compression of the liquid is due to a pressure of this order of magnitude at the interface liquid-charcoal, is supported by the very interesting work of Lamb and Coolidge,<sup>4</sup> who approach the subject from an entirely different experimental standpoint. They find that the net heats of adsorption are closely proportional to the heats of compression under high pressure, which “indicates that the liquids are all attracted by the charcoal with substantially the same force, and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres when 1 cc. of liquid is adsorbed on 10 g. of charcoal.” Still another paper,<sup>5</sup> also published later than our own, comes to the conclusion that the volume of a liquid in charcoal is different from the volume of the same mass of the same liquid in bulk.

<sup>2</sup> It is obvious that the magnitude of the mean pressure decreases as the volume of liquid considered increases.

<sup>3</sup> Donny, *Ann. chim. phys.*, 16, 167 (1846); Berthelot, *ibid.*, [3] 30, 232 (1850); Moser, *Ann. phys.*, [2] 160, 138 (1877); Helmholtz, *Ges. Abh.*, 3, 264 (1887); Worthington, *Phil. Trans.*, [A] 183, 355 (1892); Meyer, “Zur Kenntnis des negativen Druckes in Flüssigkeiten,” Halle, 1911. The heat of adsorption was discovered as a phenomenon by Pouillet nearly one hundred years ago (*Gilb. Ann.*, 73, 356 (1823)). The hypothesis that the high heat of adsorption indicates that it may be convenient to look upon adsorbed material as in a compressed state, is also very old. It is discussed in Freundlich’s “*Kapillarchemie*” (Leipzig, 1909, p. 111). However the work of the present writers gives the first direct experimental demonstration of this compression, and shows that the magnitude of the effect is much greater than has usually been supposed.

<sup>4</sup> Lamb and Coolidge, *THIS JOURNAL*, 42, 1146–70 (1920).

<sup>5</sup> A. M. Williams, *Proc. Roy. Soc. (London)*, 98A, 223–34, December (1920). The writer has not been able to consult this paper since this number has failed to reach any of the Chicago libraries.

In March 1920 Cude and Hulett<sup>6</sup> published data on the volume and density relations of one charcoal as obtained with four different liquids. It happened that at the time our preliminary paper giving data on 11 different liquids had been published, and we were somewhat disturbed to find that the agreement between the two sets of data was not as perfect as might have been desired, though the only discrepancy was for the single liquid benzene. However, on this account the publication of the present paper has been delayed for considerably more than a year. During this time Mr. C. E. Monroe has repeated a number of the determinations and has extended the investigation to other liquids for which the compressibilities have been determined by Bridgman. His results will be published in a separate paper, but it may be stated that they agree almost exactly with those of the present and also of the preliminary publication.

In the experiments presented here the charcoal was outgassed by the use of a mercury condensation pump with a large throat and connecting tube (25 mm. in diameter), but it was found necessary to constrict the tubes near the charcoal bulb to 1 cm. The apparatus first used was similar to that described by Lemon<sup>7</sup> since we had two sets of this apparatus for work on the speed of adsorption of various poison gases. However such an elaborate apparatus is unnecessary for the work on liquids, and a system without stopcocks was found to be better for this purpose. The outgassing was first conducted at low temperatures, with a gradually increase to 600°. The tubes of charcoal were kept at the latter temperature from two to three days, or until the pressure registered by the McLeod gage had fallen to 0.0001 mm. and had remained as low as this for at least 6 hours. This pressure was determined while the pump was still running, but the tubes of charcoal were connected to the main vacuum line (1.5 cm. in diameter) between the gage and the pump. The neck of the bulb, which usually contained about 10 g. of charcoal, was then sealed off to a point while the bulb was still kept hot in the electric furnace. The bulb was cooled, the point dipped under the surface of the hot liquid, and broken off, so as to allow the liquid to rise into the tube. The tube was weighed at intervals, being kept in a thermostat at 20.00° except during the periods it was kept in the balance. The surface of the liquid was so adjusted in the thermostat that the lower part of the meniscus was exactly at a fine circular graduation made on the neck of the tube where it had been constricted to a capillary. After the drift had ceased, the final data as recorded, were obtained. The character of this drift has been treated by Cude and Hulett, and will be considered by Mr. Monroe, so only the final density data will be presented here.

<sup>6</sup> Cude and Hulett, *THIS JOURNAL*, 42, 391-401 (1920). Their results on benzene are affected by some factor which we have not been able to duplicate.

<sup>7</sup> Lemon, *Phys. Rev.*, 14, 283 (1919).

## 2. Apparent Density and Volume Relations of Charcoal.

The most closely agreeing data were obtained by the use of a steam activated, coconut-shell, gas-mask charcoal E 602, which gave a service time of 47.2 minutes by the accelerated chloropicrin test. On account of the close agreement of the three or more density determinations with each liquid, in general to  $\pm 0.001$ , only the average values will be included in Table I, which gives the results for this charcoal. The density listed in Col. 2, and the pore volume given in Col. 3, are not the real, but only the apparent values, calculated on the basis that the liquids are incompressible, or what amounts to the same thing in this case, that the liquids are not attracted by the charcoal sufficiently to cause any compression. Since apparently this kind of assumption is not justified, the true density and pore volume can be calculated only when the correct interpretation of the cause of the considerable variation shown in the table, is obtained.

TABLE I.

APPARENT DENSITY AND PORE-VOLUME DETERMINATIONS FOR A STEAM-ACTIVATED COCONUT-SHELL GAS-MASK CHARCOAL.

(Charcoal E 602; service time 47.2 minutes;  $-\Delta v = 0.058$  cc.)

(Data at 25°.)

1. Liquid.	2. Apparent density.	3. Pore volume 1 cc.	4. Percent compressed 12000 at- mospheres. <sup>a</sup>	5. Surface tension, dynes per cm. $\gamma$ .	6. Viscosity in absolute units. $\eta$ .	7. $\frac{\gamma}{\eta}$ .	8. $\frac{b}{\eta} \times 10^4$ .
Mercury .....	0.865	.....	.....	57.0	.....	.....	..
Water .....	1.843	0.534	20.51	72.8	0.0101	7200	14
Propyl alcohol .....	1.960	0.559	22.93	23.7	0.0223	1062	76
Chloroform .....	1.992	0.566	.....	27.13	0.0057	4760	45
Benzene .....	2.008	0.568	.....	28.88	0.0064	4510	54
p-Xylene .....	2.018	0.571	.....	28.33	0.0064	4430	81
Petroleum ether .....	2.042	0.579	.....	.....	.....	.....	..
Carbon disulfide .....	2.057	0.580	25.75	31.38	0.0037	8480	34
Acetone .....	2.112	0.590	27.0	23.50	0.0033	7120	44
Ether .....	2.120	0.592	30.0	17.1	0.0024	7125	39
Pentane .....	2.129	0.593	More than ether	About 15	0.0024	6200	65

<sup>a</sup> The solubility of gases in these liquids increases in *general* with the percentage of compression or the compressibility, but the order is not exactly the same. The values for the density and for the pore volume listed in this table are calculated on the basis of the incorrect assumption that the liquids are incompressible. The same values would be obtained if the liquids are compressible but are not compressed. The eighth column gives the values of  $b$  of van der Waals' equation.

TABLE II.  
APPARENT DENSITIES OF EIGHT CHARCOALS IN WATER, MERCURY AND VARIOUS ORGANIC LIQUIDS.

Charcoal.	Liquid.	Apparent density.	Mean apparent density.	Volume of carbon in 1 cc. charcoal.	Volume of pores in 1 cc. of charcoal.
Charcoal A	Hg	0.843			
(Steam activated, coconut shell-charcoal; impregnated with copper; service time = 42.9 minutes; $-\Delta v = 0.052$ cc.)	Hg	0.841	0.842	.....	.....
	H <sub>2</sub> O	2.112	.....	.....	.....
	H <sub>2</sub> O	2.112	2.112	0.399	0.601
	C <sub>6</sub> H <sub>6</sub>	2.291	.....	.....	.....
	C <sub>6</sub> H <sub>6</sub>	2.298	2.295	0.366	0.643
	Ether	2.432	.....	.....	.....
	Ether	2.422	2.426	0.347	0.653
Active carbon No. 4	Hg	0.705	.....	.....	.....
(From anthracite coal and pitch; service time = 40.9 minutes; $-\Delta v = 0.067$ .)	Hg	0.713	0.709	.....	.....
	H <sub>2</sub> O	1.807	.....	.....	.....
	H <sub>2</sub> O	1.809	1.808	0.392	0.608
	Ether	2.186	.....	.....	.....
	Ether	2.172	2.177	0.325	0.675
Charcoal No. 1	Hg	0.869	0.869	.....	.....
(Air activated, coconut-shell charcoal; service time 32 minutes; $-\Delta v = 0.053$ cc.)	H <sub>2</sub> O	1.863	1.863	0.467	0.533
	C <sub>6</sub> H <sub>6</sub>	2.014	2.014	0.432	0.568
	Pet. Eth.	2.042	2.042	0.421	0.579
	Ether	2.094	2.094	0.414	0.586
E621	Hg	0.989	.....	.....	.....
(Air activated, coconut-shell charcoal; service time = 27 minutes; $-\Delta v = 0.051$ .)	Hg	0.998	0.995	.....	.....
	H <sub>2</sub> O	1.832	.....	.....	.....
	H <sub>2</sub> O	1.838	1.835	0.542	0.458
	Ether	2.023	.....	.....	.....
	Ether	2.029	2.026	0.491	0.509
Active carbon No. 1	Hg	1.177	.....	.....	.....
(from anthracite coal and pitch; service time = 19 minutes; $-\Delta v = 0.043$ cc.)	Hg	1.172	1.175	.....	.....
	H <sub>2</sub> O	1.936	.....	.....	.....
	H <sub>2</sub> O	1.932	1.934	0.609	0.391
	Ether	2.076	.....	.....	.....
	Ether	2.074	2.075	0.566	0.434
Active carbon No. 3	Hg	1.488	.....	.....	.....
(from anthracite coal alone; service time = 11 minutes; $-\Delta v = 0.018$ cc.)	Hg	1.492	1.490	.....	.....
	H <sub>2</sub> O	1.880	.....	.....	.....
	H <sub>2</sub> O	1.872	1.876	0.799	0.201
	Ether	1.911	.....	.....	.....
	Ether	1.902	1.906	0.781	0.219
Laboratory charcoal	Hg	0.521	0.521	.....	.....
(from beechwood; service time = 0.0 minutes; $-\Delta v = 0.004$ cc.)	H <sub>2</sub> O	1.644	1.644	0.317	0.683
	Ether	1.665	1.665	0.313	0.687

TABLE II (Continued).

Charcoal.	Liquid.	Apparent density.	Mean apparent density.	Volume of carbon in 1 cc. charcoal.	Volume of pores in 1 cc. of charcoal.
Cedar wood .....	Hg	0.817	.....	.....	.....
(service time = 0.0 minutes; - $\Delta v$ = 0.008 cc.)	Hg	0.813	0.815	.....	.....
	H <sub>2</sub> O	1.497	.....	.....	.....
	H <sub>2</sub> O	1.502	1.499	0.544	0.456
	Ether	1.504	1.504	0.536	0.464

In order to understand the volume and density relations upon which the adsorptive properties of charcoal depend, it is important to obtain an idea of the structural relations of coconut charcoal, insofar as the latter can be revealed by the use of the microscope. The writers have about 60 microphotographs, with magnifications as high as 2000, prepared by Dr. Rheinhardt Thiessen of the U. S. Bureau of Mines, and these have been used in the present study of the pore volume relations. Unfortunately none of these can be presented here, but reference may be made to three microphotographs reproduced in an earlier paper by Lamb, Wilson, and Chaney,<sup>8</sup> which do not, however, represent all of the types of structure found. A reference to their Figs. 7 and 8 (pp. 428 and 429) of their paper will show that the lumps of charcoal contain many pores which are visible at a magnification of 732 diameters. Those visible at a magnification of 2000 may be called capillaries or macropores. The walls of carbon, which are represented by the light portions of the figure, are undoubtedly very porous, and contain an enormous number of "micropores" which are ultramicroscopic. A study of the photographs shows that the mean diameter of the macropores is about 12 microns.<sup>9</sup> The micropores may be defined arbitrarily as those whose diameters are less than  $10^{-5}$  cm. (less than 100 millimicrons), though vapor-pressure measurements indicate, insofar as they are of any value for this purpose, that they are mostly of the order of  $10^{-6}$  cm. or less, in diameter.

Since mercury penetrates neither the capillaries nor the micropores, the density given in Tables I and II, with this liquid used to fill the "voids" between the lumps of charcoal, is that of the lumps themselves, walls, micropores, and capillaries included, or what is known as the lump or "block density." It will be seen that this density is close to 0.85 for two of the highly activated coconut-shell charcoals, but is considerably higher for the slightly activated charcoal E 621, for which the value is practically 1.000. The density of the cedar wood charcoal, 0.815, is very nearly the same, yet this specimen shows an almost zero service time, while beechwood charcoal, also a very poor adsorbent, has a block density of only 0.521. The active carbon 4, with a moderately high service time of 40.9 minutes, has a moderately low density (0.709), and the much

<sup>8</sup> Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, 11, 420-38 (1919).

<sup>9</sup> This diameter is dependent upon the methods of production of the charcoal.

less active No. 1, also made from anthracite coal and pitch, has a much higher density (1.175), while the still less active carbon No. 3, with the low service time of 11 minutes, has a very high density (1.490).<sup>10</sup>

### 3. Relation of the Total Apparent Pore Volume to the Compressibility of the Liquids.

The most remarkable feature of Tables I and II is that the apparent density and total pore (capillary and micropore) volume depend upon the liquid in which the charcoal is immersed, and in general both increase markedly either as the compressibility increases or the viscosity decreases. This suggests alternative hypotheses, which lead to practically opposite conclusions with respect to the density. The first of these, supported also by the later data obtained by Mr. Monroe, is that *the liquid in the micropores is very highly compressed by adsorption, and that this compression is greater, the greater the compressibility of the liquid in bulk.*<sup>11</sup> That the molecules of the liquid should be drawn closer to the atoms in the surface layers and edges, seems to be the normal supposition when the magnitudes of the adhesional forces are taken into account, since such forces are much more intense than those which hold the molecules of liquid together. While this may not have been proved directly, it is evident that the energy of adsorption for a charcoal surface is very much higher than the energy of cohesion in water or in an organic liquid, since the energy of vaporization of such an adsorbed liquid is very much greater than that of the liquid itself. In addition to this the work of this laboratory has shown that even on a mercury surface the energy of adhesion for these liquids is usually three or more times that in the pure liquids. It should be noted that this factor is altogether too low to express the relations at a carbon surface.

However, the compressive effect need not vary directly as the compressibility of the liquid in bulk, since the liquid is not compressed isotropically. A second factor which might be expected to cause a divergence is that the force of adhesion is not the same for all of the liquids. When these factors are considered, the agreement in the order seems very remarkable.<sup>12</sup>

When the highly evacuated lump of charcoal is put under the surface of a liquid, the latter enters the capillaries or macropores, and these in the charcoals which preserve to a considerable extent the original structure of the shell, have diameters of the order of 0.012 mm. in diameter, so they are filled quickly, provided they are in direct communication with the

<sup>10</sup> All of these data refer to the lump density.

<sup>11</sup> The second hypothesis suggested, that the most viscous liquids penetrate least, does not seem to be in good agreement with the experimental data, as indicated later in the text.

<sup>12</sup> This indicates that the variation of the adhesive force with a change from water to various organic liquids, is not very great. This agrees with the conclusion of Lamb and Coolidge (Ref. 4).

liquid, but the micropores are filled much more slowly. In the capillaries the driving force of penetration is the surface tension, while the retarding force is the viscosity, and the speed of penetration should vary as the ratio  $\gamma/\eta$  where  $\gamma$  represents the surface tension and  $\eta$  the viscosity. That this is true has recently been shown by Washburn. It might be thought that the differences in the volumes of the liquids which penetrate the charcoal are due to incomplete penetration by some of the liquids, especially in the cases of water and propyl alcohol, but there is *no parallelism* between the values of the ratio  $(\gamma/\eta)^{1/2}$  and the volume of liquid which penetrates. However, as the pores become finer the influence of the viscosity may become predominant, especially when the liquid after passing through a part of a narrow pore enters into a region where its cross section becomes enlarged.

While a consideration of the relation between the pore volumes and the viscosities of the liquids as presented in Table I, shows that the data would in general support the idea that the effects might be due to different penetrations of the charcoal by the different liquids, the least viscous penetrating most, it will be seen that the propyl alcohol is very badly out of order in this sense, though in exactly the order prescribed by the compressibility hypothesis. Since several other liquids have been found by Mr. Monroe which are also out of order with respect to viscosity, but in the order of the compressions, it seems evident that at least the greater part of the observed differences in volume is due to the compression of the liquid, though the viscosity may exert a minor influence upon them.

The apparent densities in water of the coconut-shell charcoals as given above are 1.843 and 1.863; that of the similar charcoal used by Titoff, 1.86; by Baerwald, 1.92; and by Miss Homfray, 1.66; by Cude and Hulett, 1.854 on 18- to 20-mesh, and 1.900 for the same charcoal of 100- to 200-mesh (per inch). Kerosene gave very nearly the same apparent density with charcoal E 602 as benzene, or about 2.008. With this may be compared the data obtained by Chaney and Apmann, who determined the apparent density in kerosene of 30 charcoals, and found that the lower the value of this quantity, the lower in general is the service time. Thus densities in kerosene of 2.14, 2.17, 2.11, 2.11, 2.08, 2.02 and 2.02, correspond respectively to service times of 68, 64, 60, 59, 57, 55, and 54 minutes; while at the other extreme, densities of 1.98, 1.86, 1.87, 1.66, 1.63, and 1.66, correspond to service times of 33.1, 30.7, 27.6, 17.8, 8.0, and 4.3 minutes. Their data are in good agreement with the value found here, since a density of 2.02 in kerosene, the value corresponding to Table I, was found by them to correspond to a service time of 41 to about 49 minutes, which is not very far from that given in Table I.

However, there is not such good agreement with the data obtained by Cude and Hulett,<sup>6</sup> as is shown in Table III.



TABLE III.

APPARENT DENSITIES OF TWO SPECIMENS OF COCONUT-SHELL CHARCOAL.

Liquid.	Cude and Hulett charcoal A 909 (18- to 20-mesh).	This investigation charcoal E 602 (10- to 14-mesh).
Water .....	1.854	1.843
Benzene .....	1.797	2.008
Carbon disulfide.....	1.915	2.057

The discrepancy in the sign of the difference exists only in the single case of benzene. This liquid exhibited the same relative order in our investigations of two other charcoals, A and No. 1, so its position in the series can hardly be an accident, especially as many determinations were run for charcoal E 602. Some factor was evidently present in the work of Cude and Hulett,<sup>6</sup> which was absent in our own. It is possible that the discrepancy is due to the extent of the outgassing, which was more thorough in our work, since we happened to have a very much more rapid vacuum pump, used a large connecting tube in place of their capillary, and outgassed for 3 days.

It is of interest to note that in the more active charcoals the apparent volume of ethyl ether, minus the volume of water, in the pores of 1 cc. of charcoal ( $-\Delta v$ ),—which shows how much more the ether is compressed than the water,—is nearly constant and about 0.055 cc. as is shown by Table IV.

TABLE IV.

COMPRESSION OF ETHER IN CUBIC CENTIMETERS PER CUBIC CENTIMETER OF CHARCOAL, MINUS THE COMPRESSION OF WATER ( $-\Delta v$ ).

Charcoal.	Service time, minutes.	$-\Delta v$ .
E 602 .....	47.2	0.058
Rankinite A .....	42.9	0.052
Active carbon 4 .....	40.9	0.067
Charcoal 1 .....	32.0	0.053
E 621 .....	27.0	0.051
Active carbon 1 .....	19 0	0.043
Active carbon 3 .....	1.10	0.018
Cedar wood charcoal .....	0.0	0.008
Beechwood charcoal .....	0.0	0.004

Of these charcoals the last, that made from beechwood, was the poorest adsorbent for chloropicrin as determined by the regular test. It is apparent that the value of  $-\Delta v$  is nearly constant as the service time decreases from 47 to 27 minutes, but falls very rapidly as the service time decreases to 19 and 11 minutes, while the charcoals which give practically a zero service time, give also a very small value for the compression decrement ( $-\Delta v$ ).

#### 4. The Heat of Adsorption of Liquids in Charcoal.

When lumps of outgassed charcoal are dropped into a liquid, or when a liquid is poured into a tube which already contains the charcoal, the liquid

penetrates the charcoal, with the result that the carbon surface of the pores disappears, and a carbon-liquid interface takes its place. In this process heat is developed, and this may be specified as the heat of immersion, of adsorption ( $-Q_a$ ), or of absorption. Thus 1 g. of bone charcoal, which had not been outgassed, gave off 18.5 calories when immersed in water, while the same weight of fuller's earth in the same liquid, gave 32 calories. The data of Lamb and Coolidge on the heat of adsorption of vapors by charcoal, indicate that the heat of immersion of a typical coconut-shell charcoal in carbon disulfide is of the order of 35 calories per gram.

The heat of immersion of a solid whose surface is so nearly plane that its surface energy is essentially equal to that of the same area of a plane surface of the same material, or the heat of adsorption of a liquid on the surface of the solid, may be defined in a corresponding way as the amount of heat liberated ( $-Q_a$ ) when a solid with a surface of this type, and of an area of 1 sq. cm. is immersed in a liquid in such a way as not to increase materially the area of the surface of the liquid. In this process the surface of the solid would disappear, and in its place would appear the same area of interface solid-liquid. The heat liberated ( $-Q_a$ ), would be equal to the total amount of energy given off in the process when carried out isothermally ( $E_a$ ), and this is equal to the total surface energy of the solid ( $E_s$ ), minus the total surface energy of the interface ( $E_i$ ), for 1 sq. cm. of surface. Since the total surface energy is always equal to the free surface energy ( $\gamma$ ) plus the latent heat of the surface ( $-T \frac{\partial \gamma}{\partial T} = l$ ), the following equation expresses the value of the heat of adsorption.

$$-Q_a = E_a = E_s - E_i = \gamma_s + l_s - (\gamma_i + l_i) = \gamma_s - T \frac{\partial \gamma_s}{\partial T} - \gamma_i + T \frac{\partial \gamma_i}{\partial T} \quad (1)$$

It is obvious that this equation is also valid for the heat of immersion of a liquid, or for the heat of adsorption of one liquid on the surface of another liquid, so in its more general sense the subscript *s* refers to the phase whose surface is already developed, but later disappears, giving place to an interface of the same area. The heat liberated on the immersion of a solid has always been found to be a positive quantity, which indicates that the total interfacial energy per unit area is always less, so long as this holds true, than the total surface energy of the solid. That this is not always the correct sign of the effect, at least when only liquids are involved, is shown by the fact that hexane, octane, and carbon tetrachloride have negative heats of immersion in water equal respectively to  $-0.21$ ,  $-0.21$ ,  $-0.26$ , times  $10^{-6}$  calories per sq. cm. at  $20^\circ$ , though the heats of immersion of water in these liquids are all positive,  $1.4$ ,  $1.34$ , and  $1.05$  times  $10^{-6}$  calories per sq. cm. Even in the case of two liquids heat is almost always evolved on immersion as the result of the surface energy changes. Thus, for example, the heat of immersion of normal octyl

alcohol at 20° in water is 1.28, and of water in octyl alcohol, 2.85, in terms of the units used above.

The heat liberated on adhesion ( $-Q_A$ ), and the total adhesional energy ( $E_A$ ), are always larger positive (or smaller negative) quantities than those which give the heat liberated on immersion (heat of adsorption), provided the surfaces are plane. The following equation gives the heat of adhesion.

$$-Q_A = E_A = E_s + E_l - E_i = (\gamma_s + l_s) + (\gamma_l + l_l) - (\gamma_i + l_i) \quad (2)$$

These are the same as the heat and energy of approach, since the surfaces of two phases already in existence, approach each other and disappear, while an interface, equal in area to that of either surface which disappears, takes their place. The heat of adhesion is 2.6 for water-hexane, 4.0 for water-octyl alcohol, 2.5 for water-carbon tetrachloride, all in  $10^{-6}$  calories per sq. cm. at 20°.

When a liquid spreads over a solid, the surface of the solid disappears, while an interface of the same area appears. If the solid has a plane surface, then a liquid surface of the same area also appears; so, provided the liquid layer is not too thin, the following equation holds

$$-Q_{sp} = E_{sp} = E_s - (E_l + E_i) = \gamma_s + l_s - (\gamma_l + l_l) - (\gamma_i + l_i) = E_A - E_c$$

where  $E_c$  represents the energy of surface cohesion of the liquid.

Obviously

$$-Q_a = E_a = E_A - E_l$$

or the heat liberated by the adsorption of a liquid equals the energy of adhesion minus the surface energy of the liquid. Also

$$-Q_a = E_a = E_{sp} + E_l.$$

and

$$E_{sp} = E_A - 2E_l.$$

The heat of adsorption of a saturated vapor is

$$-Q_g = (\gamma_s + l_s) - (\gamma_i + l_i) + \lambda v = E_s - E_i + \lambda v$$

where  $-Q_g$  is the heat of adsorption of enough vapor to form a liquid in bulk covering the solid surface at constant temperature, and  $\lambda$  is the latent heat absorbed in the vaporization of the liquid per unit volume of vapor. It is assumed here that the area of the surface of the liquid formed is negligible in comparison with the area of the interface which is formed.

While we do not have the values of the above quantities for carbon, they have been determined in this laboratory for the interfaces between mercury and other liquids; in which case the values for the liquid mercury may be substituted for the values for the solid in the above equations. The heat of adsorption as defined above is thus found to be 3.25 for *iso*-butyl alcohol, 2.60 for *secondary* octyl alcohol, and 3.13 for octane, all

in  $10^{-6}$  calories per sq. cm. The heat of spreading of *n*-octyl alcohol on water is about that of *iso*-butyl alcohol on mercury, but that for octane on water is less than half the similar value for mercury.

### 5. The Area of the Surface Exposed to a Liquid inside One Gram of Charcoal.

That there is anything in a lump of charcoal which corresponds to a plane surface is altogether improbable; and it is not unlikely that what corresponds to a surface may be molecularly rough, so that it would be impossible to designate any number which would correspond to the area in square centimeters of the surface. However, several estimates of this surface area have been made. Thus Lamb, Wilson, and Chaney<sup>8</sup> have estimated the surface in 1 g. of an activated charcoal as 1000 square meters, Lowry and Hulett<sup>13</sup> obtain the value 200 square meters for a similar charcoal, while A. M. Williams,<sup>14</sup> in developing a new interpolation formula for the adsorption of gases, calculated the surface of the non-activated charcoal used by Miss Homfray as 131 square meters.

The data given in the preceding section of this paper, together with the equations given there suggest an independent method of determining whether these estimates are of the right order of magnitude to represent what may be called the "apparent surface," which will be defined as the area of the plane surface of the same material which will give the same heat of immersion or of wetting when wet by the same liquid in bulk. Unfortunately for our purpose the heat of adsorption of charcoal has been determined in none of the liquids given there, so what will be presented here will be merely illustrative of the method. We will suppose that the heat of immersion of charcoal in carbon disulfide is as large or larger than the heat of immersion of mercury in octane, which does not seem unreasonable. If we assume that these two heats of immersion or of wetting are equal, the heat of immersion of one gram of charcoal in carbon disulfide, 35 calories, would correspond to an *apparent area* as defined above of about 120 square meters. Since it is practically certain that the heats of immersion of carbon are higher than those for mercury, this result would seem to represent a maximum which is still too large. The method of calculating the area of the charcoal surface by the use of the capillary equation of Anderson<sup>15</sup> cannot be expected to give any real correspondence with even such an apparent area, since his equation obviously breaks down completely at the diameters of the micropores which are calculated from the equation. Thus Lowry and Hulett<sup>13</sup> by using his equation find  $1.6 \times 10^{-8}$  cm. as the minimum, and  $8.3 \times 10^{-7}$  cm. as the maximum diame-

<sup>13</sup> Lowry and Hulett, *THIS JOURNAL*, **42**, 1393-1419 (1920).

<sup>14</sup> A. M. Williams, *Proc. Roy. Soc. Edinburgh*, **39**, 48-55 (1918).

<sup>15</sup> Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

ters of the pores in all of the charcoals investigated by them; and calculations from data obtained in this laboratory give values of the same order but without the above minimum. These dimensions are of such a small magnitude as to approach so closely molecular dimensions, that an equation such as the one cited, developed from the relations in a capillary tube of ordinary dimensions is altogether without meaning. However, if the lower limits for the diameter at which it is still valid could be determined, it would be useful in calculating how much of the liquid is contained in pores of that and smaller diameters. Experimental work of the heat of immersion of porous solids in liquids was begun in this laboratory several years ago, but was interrupted. It will be resumed in the coming summer.

## 6. Volume of the Pores, and the Density of Charcoal.

If either charcoal E 602 or No. 1, for which the data are very nearly identical, is taken as a characteristic coconut-shell charcoal, it may be easily seen that if the liquids are compressed by the charcoal, the total pore volume is less than even the volume of the least compressible liquid which enters the pores, when the latter is measured before the penetration occurs, as was done in the experiments. Thus the total pore volume for E 602 is less than 0.534 cc. per cc., and in the case of No. 1 it is less than 0.533. Since the macropores have diameters of the order of  $1.2 \times 10^{-3}$  cm., it is evident that in them the liquids are not materially compressed, so practically the whole of the compression occurs in the micropores.

Experiments upon the adsorption of benzene show that these charcoals adsorb about 0.39 cc. of liquid benzene, 0.35 cc. of water, 0.41 cc. of ether, etc., as measured before adsorption. From this result, together with the data on the adsorption of liquids it may be calculated that the volume relations for these charcoals are approximately 0.54, 0.28 and 0.18 for the volume of carbon (volume not occupied by liquid), volume of micropores, and volume of macropores, respectively.

These values give a density of 1.60 for the active charcoal. It may be noted that the two specimens of wood charcoal which showed almost no compressive action on the liquids, those from beech and cedar wood, had densities equal to 1.65 and 1.50 respectively, or not far from the estimated value for the carbon in the coconut-shell charcoal.

While Table I does not give any values for liquids whose percentage compressions have been determined directly at 12,000 atmospheres as lying between that of propyl alcohol and that of carbon disulfide, the determinations on the compressibility of liquids at lower pressures indicate that chloroform, benzene, and *p*-xylene are in the proper order. Mr. Monroe's paper will remedy the apparent deficiency, since he has determined the pore volumes for 5 liquids which lie in this range; amyl alcohol, isobutyl

alcohol, ethyl iodide, and ethyl and methyl alcohols. His results give extremely strong additional evidence in favor of the compression hypothesis here presented.

## 7. The Small Effects of the Size of the Molecules, and of Unequal Adhesional Attractions.

Calculations made on the relation between the lowering of the vapor pressure produced by charcoal and the size of the micropores indicate such small dimensions for the latter as to suggest that the size of the molecules might be an important factor in determining the amount of liquid which will enter them. This idea occurred to the writers early in the work, and was suggested to them repeatedly by others. However, although a number of liquids were chosen with the purpose of varying the molecular size considerably, this effect is not so large that it has been possible to detect it as yet. In this connection a determination of the pore volume was made with mesitylene, a liquid whose molecules are very large. For the liquids used the values of  $b$  of the van der Waals' equation varied from  $14 \times 10^{-4}$  for water to  $88 \times 10^{-4}$  for mesitylene, which indicates a considerable variation in molecular size. Also it would seem that the force of compression might vary with the nature of the adsorbed liquid, which would indicate that the percentage compressions considered should not be taken at a fixed pressure as was done in Table I. It is evident from the data published here, and even more so from other data to be published later, that these two effects considered in this paragraph are so small as to be obscured by the compression itself.

## Summary.

1. This paper gives evidence in favor of the hypothesis proposed earlier by the writers, which is that *the liquids which penetrate into charcoal are compressed by the action of a force, due to molecular attraction, which acts as a pressure of many thousand atmospheres*. In the earlier paper it was estimated that the pressure corresponded to twenty thousand atmospheres or more. The present paper indicates that it is the liquid in the micropores and not in the macropores which is compressed. On this basis the pressure would probably be considerably higher than the previous estimate, since at that time only the total pore volume was known and considered. Not only charcoal, but also all other porous substances, such as porous ceramic materials, and also very fine powders, should exert this compressive effect, but in general to a much smaller extent. The remarkable feature of the experiments listed is that they demonstrate the compression by direct measurements of the volume changes in the liquids. Experiments on the internal pressure of liquids have not succeeded in demonstrating pressures higher than 72 atmospheres.

2. Ether, which is much more compressible than water, occupies a volume in the charcoal which is about 10% less than that occupied by the amount of water which is, outside the charcoal, equal in volume to the ether. It seems probable that the water in the micropores is compressed by about 25%, or even more, while the ether is compressed by about 40%. It is evident that the liquids in the macropores, of the order of  $1.2 \times 10^{-3}$  cm. in diameter, are not compressed sufficiently to produce any noticeable effect upon the volume.

3. The true volume relations in 1 cc. of a characteristic coconut-shell charcoal may be estimated as: volume of micropores, 0.28 cc.; of macropores, 0.18 cc.; of carbon, 0.54; which gives a density of about 1.60 for the carbon. The density of the lumps of such a charcoal is about 0.868, though this lump or "block" density is as high as 1.49 for a charcoal made from anthracite coal, and as low as 0.52 for a wood charcoal.

4. The charcoals which are inactive as adsorbents of gases do not exert a compressive effect upon the adsorbed liquids of a sufficiently great magnitude to be very evident, though there seems to be a slight effect of this nature.

5. The densities of the carbon in the two inactive wood charcoals investigated are 1.65 and 1.50, which is not very far from the estimated density for the carbon of the active charcoals. It is evident that charcoals from which the hydrocarbons have been imperfectly eliminated, may have much lower densities still.

6. When coconut-shell charcoals alone are considered it is found that in agreement with the data obtained by Chaney and Apmann, the lower the apparent density in an organic liquid, the less is the adsorptive action on vapors. The present investigation indicates that this relation may be expected to hold the better the more compressible the liquid which is absorbed, so either ether or pentane or another highly compressible liquid should be used in such tests.

7. Simple thermodynamic equations are given for the heat of immersion or adsorption of a plane surface. While there is probably no definite area of surface inside a lump of charcoal, a definition for an "apparent area" may be given. The one chosen here is that the "apparent area with respect to the heat of immersion" is the area of the plane surface of carbon which will develop the same amount of heat on immersion as is equal to that developed by the immersion of 1 g. (or 1 cc., if such a different unit is preferred) of the charcoal in the same liquid. Since the "film" in the charcoal is probably a number of molecules deep, this apparent area is probably larger than corresponds to the carbon surface. Nevertheless, this method of consideration gives rise to a lower estimate of the area than the others which have been given in the literature. Thus it is in-

licated that the apparent area defined in this way is less than 120 sq. meters per gram of charcoal.

8. The magnitude of the heat of immersion of liquids on mercury is  $3.13 \times 10^{-6}$  calories for octane and  $3.25 \times 10^{-6}$  calories per sq. cm. for *iso*-butyl alcohol.

The next two papers of this series will present additional data similar to those given here, and also on the amounts of different vapors adsorbed by the charcoals used in this investigation. These data will make it possible to calculate in much more detail the pressure and cohesional relations involved.

The writers wish to thank Mr. Chaney for preparing several special charcoals for use in this work, and to express their indebtedness to the Wolcott Gibbs Fund of the National Academy of Sciences for a grant which was used in the purchase of vacuum apparatus. While the grant was made for researches upon the cobalt ammines, the apparatus was diverted from this latter work during the war period.

The compressibility data used in this paper are those of Bridgman.<sup>16</sup> Without the results of his remarkable investigations at high pressures, the evidence in favor of the compression hypothesis developed by the writers would have been much less convincing.

Note added Oct. 26, 1921.

Washburn<sup>17</sup> has devised a method for determining the "true" volume of the pores in a ceramic material by the use of a gas, such as hydrogen or helium, as the fluid for filling the pores. This method has been tried in this laboratory, and has been found to be much less simple when applied to charcoal, but it will undoubtedly give consistent results when sufficient care is taken. The data obtained thus far will not be published until they are more carefully verified. With accurate data of this nature it may be possible to calculate more exactly the pore volume and the density of charcoal, though, on account of the small size of the molecules of helium the volume of the pores penetrated by this gas may be greater than that penetrated by the larger molecules of an organic liquid. Also it seems apparent that even at ordinary temperatures the density of the helium gas is not the same in the micropores as in the free gas, that is, there is a small amount of adsorption.

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<sup>16</sup> Bridgman, *Proc. Am. Acad. Arts Sci.*, 49, 3-114 (1913); 48, 309-362 (1912).

<sup>17</sup> Private communication from Professor E. W. Washburn. Note added October 26, 1921.



[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE SEPARATION OF THE ELEMENT CHLORINE INTO ISOTOPES (ISOTOPIC ELEMENTS).

### The Heavy Fraction from the Diffusion.

BY WILLIAM D. HARKINS AND ANSON HAYES.

Received May 2, 1921.

### Introduction.

This paper will describe the experimental work begun in the year 1915 in this laboratory for the purpose of demonstrating the correctness of the hypothesis advanced by Harkins and Wilson. This was that chlorine, magnesium, and silicon, as well as neon, are mixtures of isotopes.<sup>1</sup> That neon contains an isotope of atomic weight 22, had already been discovered by Thomson<sup>2</sup> by the use of the positive-ray method, but at the time when this investigation was begun it did not seem that its presence in neon had been demonstrated by sufficient experimental evidence to make its existence altogether a certainty.<sup>3</sup> It appeared important, therefore, to demonstrate the existence of isotopic forms of at least one of the *light* elements by making an actual separation of one of the above mentioned elements into at least two fractions which would differ in their atomic weights, as determined by some chemical method. The prediction of the existence of the isotopes of the specific light elements mentioned above, was made on the basis of their chemical or mean atomic weights, and at that time the atomic weight of silicon was not known with a high degree of precision, while the atomic weights of magnesium and of chlorine, especially the latter, were considered to be very exact. For this reason and also because the deviation of the atomic weight of chlorine from a whole number is the largest known for any light element, it was decided<sup>4</sup> to attempt the separation of chlorine into its isotopes.

Of the methods suitable for the separation of substances of almost identical chemical properties such as isotopes either diffusion or the use

<sup>1</sup> Harkins and Wilson, *THIS JOURNAL*, 37, 1371, 1390 (1915).

<sup>2</sup> Thomson, "Positive Rays of Electricity," Longmans, Green and Co., London, 1913, pp. 114-5.

<sup>3</sup> A letter of the date May 5, 1915, from the Cambridge laboratory written by Dr. F. W. Aston, states "For my own part I am fairly confident of the existence of neon and meta-neon, but I do not consider the results so far warrant a definite statement to the public. It is a pity that several authors of text-books seem to have jumped to the conclusion that such has been made." In December 1919 Aston secured good evidence from the positive-ray method that Thomson's discovery was correct, and that meta-neon of atomic weight 22 exists.

<sup>4</sup> Harkins and Hall, *THIS JOURNAL*, 38, 53 (1916). The work was begun, however, by Harkins and Turner.

of a centrifugal machine seemed to give promise of the quickest attainment of results. Attempts were made to obtain funds for the construction of a centrifugal machine, since it seemed that a properly designed centrifuge might effect a comparatively rapid separation, but, since these attempts were unsuccessful, work was begun on a diffusion through the stems of church-warden pipes, as has been described by Harkins and Turner. A notice of the beginning of the experimental work was published in the year 1916.<sup>5</sup>

Not only was an apparatus constructed for the separation of chlorine, but Turner also built an apparatus containing about 12.2 meters of porous pipe stems, which was used in diffusing large quantities of hydrogen chloride. The diffusions were interrupted by the war, though a considerable amount of the latter gas was diffused by T. H. Liggett during the year 1917-8. In the autumn of 1919 the work was taken up by C. E. Broeker, who diffused fractionally both the light and heavy fractions. Preliminary analyses on the heavy fraction indicated that its atomic weight had been increased to 35.51, or by 0.05 unit, in February 1920, and a preliminary notice of the separation was published in the February, 1920, number of the *Physical Review*,<sup>6</sup> in *Science*,<sup>7</sup> and in *Nature*.<sup>8</sup> This seems to be the first separation of an element into isotopes, for which there is any satisfactory evidence, but attention should be called to the fact that Aston in 1913 made a preliminary report to the British Association on an attempt to separate neon into isotopes. Since he has not published the details of this work at any time, it is impossible to know what was accomplished, but Aston himself states that the results were not at all conclusive.<sup>9</sup> When the difficulties in purifying and handling neon,

<sup>5</sup> *THIS JOURNAL*, 38, 53 (1916).

<sup>6</sup> *Phys. Rev.*, 15, 74 (Feb. 1920).

<sup>7</sup> *Science*, N. S., 51, 289-91 (1920).

<sup>8</sup> *Nature*, 105, 230-1 (1920). A later note in *Nature*, Sept. 30, 1920, states that Brönsted and von Hevesy have succeeded in obtaining a difference of 1 part in twenty thousand in the density of mercury. This is less than one-thirtieth of the separation obtained earlier by Harkins and Broeker in the case of chlorine. A later paper in *THIS JOURNAL*, will show that Mulliken and Harkins have secured a separation of the isotopes of mercury more than twice as large as that reported by Brönsted.

<sup>9</sup> Aston, *Phil. Mag.*, 39, 450-51 (1920), states that in his early experiments he obtained a density difference of about 0.7, which would amount to 0.14 unit difference in atomic weight, provided no impurities were present. He states that his results were positive but not conclusive, and that in his later more elaborate apparatus he secured a density difference of only about 3/7 of the above amount, presumably because he used too great pressures in his apparatus. Aston's original report, *Report Brit. Assoc. Adv. Science*, 1913, p. 403, gave no details concerning this work. The higher value reported by Aston is altogether unreasonably large, if the theory of diffusion is taken into account, if the amount of neon produced was sufficient to be subjected to purification, since it would represent a cut of 470 thousand with a 100% efficiency. Thus even 10 liters of neon would give only 0.02 cc. While this amount might be increased by using

and the difficulty of detecting impurities, are compared with the relatively easy purification of hydrogen chloride, it will be seen that a difference of 0.05 in the atomic weight of chlorine is more conclusive than several tenths of a unit for neon, particularly when the neon is obtained, as in Aston's experiments, in very minute quantities.

In a recent note in *Nature* Aston<sup>10</sup> gives the impression that the separation of chlorine by ordinary diffusion methods is almost impossible, and considers that if we have obtained any separation it is very remarkable, since in the case of neon, where the separation is extremely difficult, only the 21st root is involved, while with chlorine it is necessary to "grapple with the 36th root." It should be pointed out that in considering only the roots involved Aston has come to a conclusion which is partly erroneous, since actually (see Table I) *a smaller cut is required to produce an increase of 0.05 in the atomic weight of chlorine than to produce the same increase in the atomic weight of neon.* Here the cut (C) is defined as the amount of the gas which passes into the diffusion tubes, divided by the amount of heavy fraction which is obtained after the diffusion. Thus, even apart from the great difficulty of securing a considerable quantity of pure neon, and the difficulties involved in keeping it pure, the theory indicates an additional disadvantage of neon for separations of this magnitude. However, as the deviation of the atomic weight increases the theory becomes more favorable to the neon, though the rarity of this gas and the other disadvantages mentioned above, together with the much smaller degree of precision in the determination of its atomic weight, more than counterbalance the advantages which arise.

The following table gives the values of the cut necessary to increase the atomic weight of chlorine and of neon by definite amounts, as calculated from the theory of Rayleigh, which relates to an ideal diffusion at low pressures into a vacuum.

TABLE I.

VALUES OF THE CUT  $(X + Y)/(x + y)$  NECESSARY FOR THE INCREASE OF THE ATOMIC WEIGHTS OF CHLORINE AND OF NEON BY DEFINITE AMOUNTS. A DIFFUSION OF THE HEAVY FRACTION. (Chlorine diffused as hydrogen chloride.)

(Percentage of isotope of atomic weight 37 in chlorine = 23, of atomic weight 22 in neon = 10.)

Increase of atomic weight.	Cut.	Chlorine. Corresponding enrichment.	Cut.	Neon. Corresponding enrichment.
0.05	160	1.1459	217	1.286
0.10	18,600	1.302	19,600	1.588
0.15	1,690,000	1.469	991,000	1.909
0.20	117,000,000	1.648	33,000,000	2.25

fractional diffusions it would seem practically impossible to secure the atomic weight change claimed upon enough material to allow of its proper purification with the amounts of neon at that time available.

<sup>10</sup> Aston, *Nature*, 105, 131 (1920).

Here  $x$  and  $y$  represent the number of mols of the light and heavy isotopes respectively in the heavy fraction after the diffusion, while  $X$  and  $Y$  represent the initial mol numbers. This table points out the important fact that it is easy to obtain an increase of 0.05 in the atomic weight of a *small quantity* of chlorine or of neon, and that it is also easy to obtain *very small quantities* of either with an increase of 0.10, provided the process is nearly 100% efficient in terms of the Rayleigh theory. However, if only very small quantities of the material are obtained, it is very difficult to make the thorough purifications which are necessary to give evidence that a separation has been effected. The table also shows that to attain an increase of 0.20 unit in the atomic weight, is very difficult, since to secure this by diffusing the heavy fraction in one operation would require that 130 tons of hydrogen chloride gas or 36 tons of neon be used provided one gram of product is to be obtained. While these amounts may be reduced considerably by the use of a system of fractional diffusions, this procedure, when used on gases, becomes very expensive either in terms of the original complications in the apparatus, or in the amount of labor necessary to keep a single system in operation.

In the above table the necessary enrichment ratio ( $r$ ) corresponding to the required change of atomic weight is equal to the value of  $(y/x)/(Y/X)$ . The equation of Rayleigh is

$$\frac{1}{C} = \frac{x+y}{X+Y} = \frac{X}{X+Y} r^{\frac{\mu}{\nu-\mu}} + \frac{Y}{X+Y} r^{\frac{\nu}{\nu-\mu}} \quad (1)$$

where  $\mu$  and  $\nu$  represent the diffusion coefficients of the light and heavy constituents respectively. This is easily converted into the form

$$\frac{Q}{Q_0} = \frac{1}{C} = r^{\frac{\mu}{\nu-\mu}} \left[ 1 + \frac{Y}{X+Y} (r-1) \right] \quad (2)$$

If it is assumed that the rates of diffusion of the gases vary inversely as the square roots of their molecular weights, this reduces to the following simple form.

$$\frac{1}{C} = r^{\frac{\sqrt{M_h}}{\sqrt{M_l}-\sqrt{M_h}}} \left[ 1 + h_0 (r-1) \right] \quad (3)$$

in which  $h_0$  represents the fraction of the heavy isotope  $Y/(X+Y)$  in the initial mixture, and  $M_l$  and  $M_h$  are the molecular weights of the light and heavy components of the mixture.

#### Relation between the Atomic Weights and Percentages of Two Isotopes and the Atomic Weight of the Mixture.

In order to calculate the cut necessary to produce a certain change in the atomic weight of a mixture of two isotopes, it is necessary to know

the fraction of each in the mixture, and this may be calculated from the mean atomic weight and the atomic weights of the pure isotopes. Let  $h_o$  and  $l_o$  represent the initial fractions of the heavy and light isotopes,  $h$  and  $l$  the similar values necessary to produce the required enrichment ( $r$ ), and  $M$ ,  $M_h$ , and  $M_l$ , the molecular weights of the mixture, of the heavy, and of the light fractions.

Then

$$l \cdot M_l + (1-l) M_h = M.$$

or

$$l = (M_h - M) / (M_h - M_l). \quad (4)$$

Similarly

$$(1-h) M_l + h M_h = M.$$

or

$$h = (M - M_l) / (M_h - M_l). \quad (5)$$

Divide (4) by (5):

$$r = \frac{h/l}{h_o/l_o} = \frac{M - M_l}{M_h - M} \cdot \frac{M_h - M_o}{M_o - M_l}. \quad (6)$$

By the use of Equations 3 and 6 the calculation of the cut necessary to produce any possible desired increase in atomic weight is very simple. It is obvious that the two equations may be combined into one.

$$\frac{Q_o}{Q} = \frac{1}{C} = \left[ \frac{M - M_l}{M_h - M} \cdot \frac{M_h - M_o}{M_o - M_l} \right] \frac{\sqrt{M_l} - \sqrt{M_h}}{\sqrt{M_l} - \sqrt{M_h}} \left[ 1 + h_o \left( \frac{M - M_l}{M_h - M} \cdot \frac{M_h - M_o}{M_o - M_l} - 1 \right) \right]. \quad (7)$$

If we let  $k$  represent  $\frac{\sqrt{M_h}}{\sqrt{M_l} - \sqrt{M_h}}$  the "diffusion exponent," then the diffusion equation reduces to the simple form:

$$\frac{1}{C} = [1 + h_o (r-1)] \times r^k. \quad (8)$$

The value of the diffusion exponent ( $k$ ) as thus defined is  $-37.503$  for the isotopic forms of hydrogen chloride provided the only isotopes have molecular weights 36.008 and 38.008, while for neon it has the value  $-21.488$ , provided the only isotopes have atomic weights 20 and 22. It may be noted that the values of the diffusion exponents are not very different from the mean molecular weights, but that this is not a general relation unless the isotopes differ in atomic weight by 2, is shown by the fact that the exponent for lithium, with atomic weight 6 and 7, is  $-13.48$ . The exponent for the isotopic forms of hydrogen bromide of molecular weights 80 and 82 (bromine of atomic weights 79 and 81) is  $-81.492$ . A convenient rule for keeping in mind the magnitude of the exponent is that it has a value equal to half a unit more than the mean of the molecular weights of the isotopes when the two molecular weights differ by 2. Thus for isotopes of atomic weights 223 and 225, the exponent is  $-224.5$ . Obviously the exponent has larger values when the difference between the iso-

topes is only 1, and smaller values when it is greater than 2. When the difference is 1 the exponent is equal to half a unit more than *twice* the mean of the atomic weights, and when it is 4, it is equal to half a unit more than *one-half* the mean.

Equation 8 may be put in the form

$$\frac{1}{C} = \left[ 1 + l_0 (r-1) \right] \times r^{k+1} \quad (9)$$

or

$$\frac{1}{C} = r^{\frac{\sqrt{M_l} - \sqrt{M_h}}{\sqrt{M_l} + \sqrt{M_h}}} \left[ 1 + l_0 (r-1) \right] = r^{k'} \left[ 1 + l_0 (r-1) \right]. \quad (10)$$

The numerical value of  $k'$  is always one unit less than that for  $k$ , and the mean of these two values is for two isotopes equal to the mean of the molecular weights when the molecular weight difference is 2, twice the mean of the molecular weights when this difference is 1, and one-half the mean of the molecular weights when this difference is 4, or

$$\frac{k + k'}{2} = \frac{M_l + M_h}{M_l - M_h} \quad (11)$$

and

$$k + k' = 1. \quad (12)$$

This relation becomes less exact as  $M_l + M_h$  becomes smaller, and as  $M_l - M_h$  becomes larger numerically. That it is sufficiently exact for accurate calculations is shown by the fact that the value of  $k$  calculated above (by the use of 7-place logarithms) in the case of hydrogen chloride is  $-37.503$ , while the value given by Equations 11 and 12, is  $-37.504$ .

In superficial discussions of the separation of isotopes there has been a tendency to concentrate the whole attention upon the diffusion exponent, and the effect of the initial percentages of the isotopes in the mixture has been neglected. That these percentages have a very marked effect upon the enrichment ( $r$ ) necessary to produce a certain change of atomic weight, is obvious. For example an infinite value of the enrichment ratio will serve to increase the atomic weight of lithium only from 6.94, the mean value, to 7.00, that for the heavier isotope so, for larger atomic weight differences for this element, the diffusions must be carried out upon the light fraction. In spite of the fact that the heavier isotope of this element has an atomic weight higher by 16.67% than that of the lighter isotope, a very high percentage difference, the theory does not indicate that the conditions for the separation are very favorable, since the enrichment ratio has a very large value. It is obvious that when a mixture of isotopes is divided into two equal parts by diffusion, the decrease of the mean atomic weight for the light fraction is equal to the increase for the heavy fraction. The equations for the light fraction are being worked out in this labora-

tory, and will not be discussed further here as they will be presented in a later paper to be published in *THIS JOURNAL* by Mulliken and Harkins. The relations have been tested by an experimental partial separation of mercury into two fractions, one of lower and one of a higher density than ordinary mercury. The most favorable proportion for the separation of a mixture of two isotopes is 50% of each. Thus, it has been found that a cut of 18,600 is necessary to increase the atomic weight of chlorine from 35.46 to 35.56, an increase of 0.1, in case hydrogen chloride is diffused. The percentage of heavy isotope in this ordinary chlorine is 23. Now it is quite remarkable that if the initial mixture contained 50% of each isotope, the same increase in atomic weight would be brought about with a cut less than  $\frac{1}{10}$  as great, or of 1,670.

Since the percentage of the heavy isotope in the heavy fraction of both chlorine and neon approaches more closely to 50% as the diffusion proceeds, the separation becomes more and more easy when considered in terms of the cut (though much more difficult in the sense that the amount of material available decreases rapidly.) Thus while the first  $\frac{1}{10}$  of a unit increase in the atomic weight of chlorine requires a cut of 18,600, the second requires only one of 6,300, while the corresponding values for neon are 19,600 and 1,710, so the second increase of 0.1 unit in the atomic weight of neon requires only  $\frac{1}{10}$  the cut. However, from the practical standpoint the great number of fractional diffusions necessary to keep the quantity of material large enough to proceed with the operations, makes each successive  $\frac{1}{10}$  unit increase very much more difficult to attain.

#### Apparatus for the Diffusion of Gases at Atmospheric Pressure.

Of the methods for the diffusion of a gas through a porous wall, there is little doubt that the most efficient is what is termed a vacuum diffusion, in which the gas diffuses through the wall into as high a vacuum as can be maintained. The pressure on the high pressure or "heavy fraction" side of the wall is kept at a magnitude which is dependent upon the diameter of the pores in the wall, and at such a value (for example 10 mm. of mercury) that the mean free path of the gas is as great as the diameter of the pores, which should be a uniform diameter. The low pressure of the gas insures not only a molecular passage of the gas through the pores, but it also aids greatly in securing a good mixing of the gas.

There are, however, several objections to the diffusion at low pressures: (1) it is difficult to make the process automatic; (2) the volume of the gas per unit mass is greatly increased; and (3) it necessitates a more cumbersome method of collecting the heavy and light fractions. For these reasons it was decided, since a fair efficiency had been obtained in a separation of known gases, and particularly since a very good (about 60%) efficiency had been obtained in the separation of the isotopes of chlorine by Mr. Broeker

by diffusing at atmospheric pressure, to delay the use of the vacuum method until after the difference in atomic weight of the chlorine separated by this method had been definitely established by the use of this partly automatic apparatus.

The general procedure adopted is to generate hydrogen chloride at atmospheric pressure by dropping conc. sulfuric acid into conc. hydrochloric acid from a height of about 90 cm.,—in order to secure good mixing of the acids. After the first diffusion the sulfuric acid was dropped upon sodium chloride. The dried gas is passed through porous porcelain tubes, and the lighter fraction which consists of the diffusate which passes through the walls is swept away by a rapid current of purified air. The heavy fraction is that which passes through the system of tubes and remains inside. Both fractions are absorbed by condensation in the *surface* of a considerable amount of water. The apparatus though quite similar to that used in this laboratory by Dr. Turner and by Mr. Broeker, but not described by them, is greatly improved in many particulars. It was designed to care for 1000 liters of hydrogen chloride per day, at atmospheric pressure.

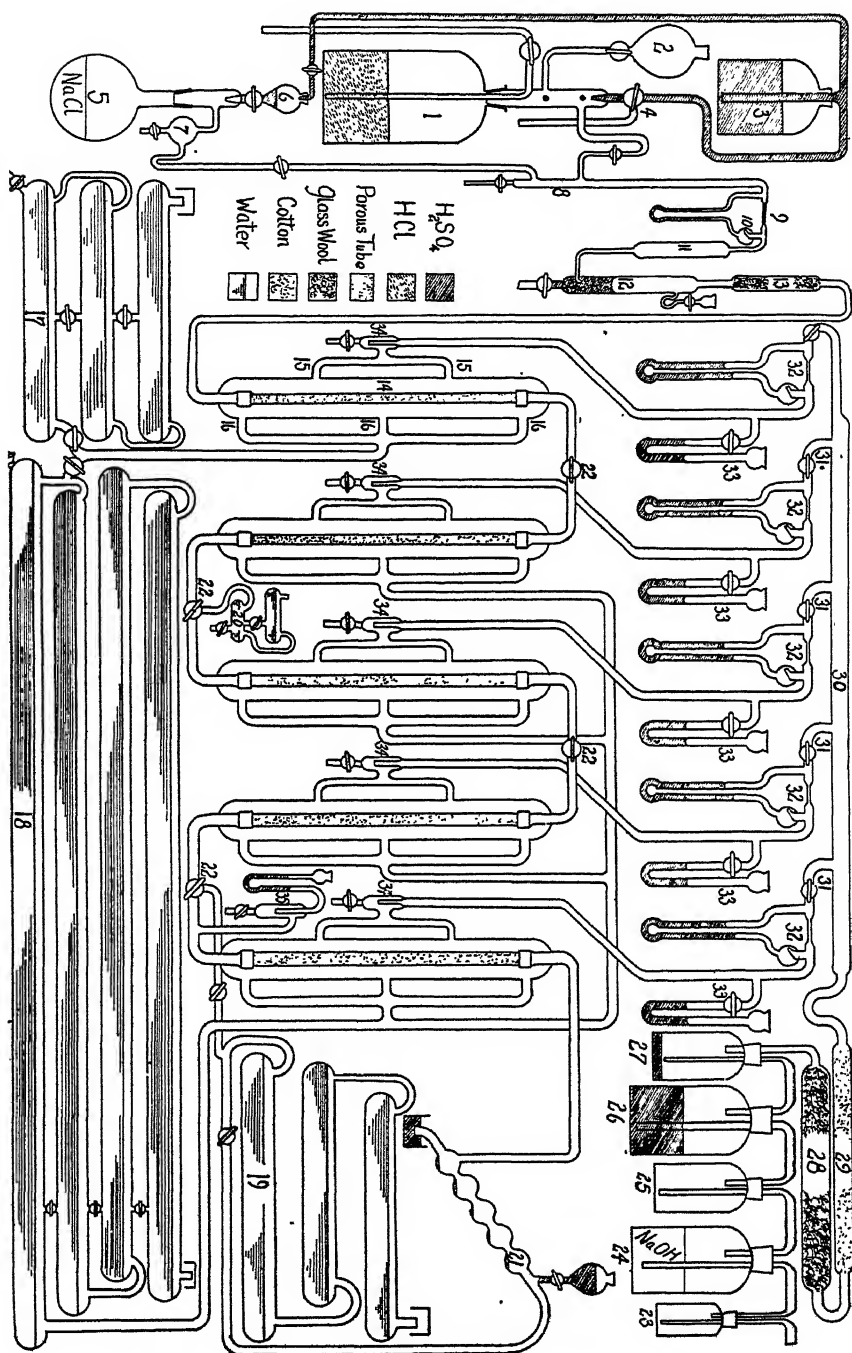
Only acids of high purity were used in the work, and the hydrogen chloride produced came in contact with only pure sulfuric acid, glass, porous porcelain, and a very small area of paraffin, from the time it left the generators until it was absorbed in distilled water of the "conductivity" grade.

Since according to the Rayleigh theory the enrichment of the heavy fraction with respect to the heavy constituent depends only upon the fraction of the original gas that remains inside the diffusion tubes, and since this fraction changes very rapidly with the rate at which the gas is fed into them from the generator, a flow meter was placed in the line leading from the generator, and the evolution of gas was so regulated that the flowmeter gave a constant reading.

Flowmeters were also placed in all of the air sweep-out lines for each diffusion tube jacket, since it was necessary to reduce the partial pressure of the hydrogen chloride in the diffusate to a very low value as soon as it escapes from the walls of the diffusion tubes, and since otherwise a back diffusion will greatly lower the efficiency of the process.

A 20-liter bottle (1), with a tall dropping head, serves as a generator for the first diffusion. Six liters of c. p. hydrochloric acid is introduced into this bottle through the dropping funnel (2). For each 6 liters of this acid about 8 liters of conc. c. p. sulfuric acid is dropped into it from a very wide 24-liter supply bottle (3). The flow of acid after it is started, is controlled by the 3-way stopcock, (4), the supply being sufficient to run for 23 hours. By refilling the generator at about 4.00 P.M. each day, a very steady flow of gas is secured through the night, the regulation requiring no attention between 10.00 P.M. and 7.30 A.M. When the speed of generation begins to fall in the morning, the generator is heated to 50° by means of an air-bath heated on an electric hot plate. By this means 75% of the hydrochloric acid in the original acid can be





recovered. The generator is emptied by means of pressure through the siphon (4) directly into a carboy. For all succeeding diffusions the gas is generated in a 2-liter or a still smaller flask (5) into which sulfuric acid is dropped from a funnel (6). When the speed of evolution of gas from this generator falls, it is heated to 100°, thus giving nearly 100% recovery of the hydrogen chloride.

The trap (7) is to prevent an explosion of the generator, which otherwise is likely to occur if the generator happens to foam over, since the warm sulfuric acid solution of sodium hydrogen sulfate will solidify very quickly when it reaches the cold tubes. This usually clogs the tubes, and an explosion is apt to result, but has never occurred when the trap is in the system.

From the generators the hydrogen chloride passes into the trap (8) which collects moisture and sulfuric acid spray and through the flowmeter (9). Sulfuric acid is used as the manometer liquid in all of the flowmeters, and its injection into the apparatus is prevented by the traps (10). The bulb (11) is used to prevent sulfuric acid from being drawn back into the flowmeter (10) from the gas dryer (12). The thistle tube and its connections on (12) served to introduce fresh acid into the dryer, and also as a manometer to measure the pressure at the generator end of the diffusion train. The drying acid in (12) is renewed every second day. The bulb (13) is filled with glass wool, tightly packed, to filter out all sulfuric acid spray from the dried gas. After passing this the gas goes directly into the first diffusion tube (14). The first diffusion tubes are the stems of churchwarden pipes, while the succeeding ones were especially prepared for our use by the Ceramics Division of the Bureau of Standards. The latter are one meter long, 11 mm. outside diameter, with 2 mm. walls. They are sealed into glass tubes of almost the same diameter by the use of plaster of Paris. The diffusion tubes were then sealed into glass jackets 1.5 meters long, and 5 cm. in diameter. The air for sweeping out the diffusate enters the jackets through the two tubes (15) and passes out of it through the three tubes (16). These three exit tubes for each jacket are assembled into a single line leading to the absorbers for the light fraction. During the first diffusion the material from the first diffusion unit is absorbed in distilled water in absorber (17) and is designated as the light fraction from the first diffusion. During later diffusions of the heavy fraction this absorber is shunted out of the line, since its capacity is too great. The diffusate from the succeeding 4 jackets is absorbed in the large absorber (18) and when the concentration of the solution reaches 6 *N*, it is turned back into the stock of the laboratory (not, however, for any diffusion after the first) as dil. chemically pure hydrochloric acid. It is free from sulfites, sulfates, organic matter, and gives no test for iodine or bromine. The heavy fraction, or that which remains inside of the tubes at the end of the fifth or last unit, is absorbed in the absorber (19).

In the third and fourth diffusions only the first two units are used, and the small absorber (20) is used for the heavy fraction. Very large 3-way stopcocks (22) are between each two diffusion units, so that the apparatus may be used as two or more separate diffusion trains. The series of bulbs and the dropping funnel (21) constitute a sulfuric acid dryer for the heavy fraction passing from the fifth unit to the absorber (19), its purpose being to prevent any moisture from the absorber from reaching the porous tubes. The absorbers were all made on the same plan, and consist of two or more horizontal, and usually very large, glass tubes, arranged one above the other. Each of these tubes is provided with a gas inlet tube at one end, and an outlet tube at the other, and also with a tube and stopcock for allowing the acid to be dropped into the next unit below, or, on the bottom or first unit, for drawing it off from the apparatus.

The horizontal tubes are filled nearly full of pure distilled water thus leaving a long narrow passage for the gas. Nearly all of the hydrogen chloride is absorbed in the first unit, and none of this gas can be detected by the odor at the exit from the last tube.

When the solution in the first or bottom tube reaches 6*N* in concentration, it is drawn off, the solution in each of the other tubes is dropped into the tube just below it, and distilled water is poured into the last or uppermost tube. This change can be made during the operation of the apparatus, while the method of surface absorption makes it possible to keep the pressure in the tubes very close to that of the external atmosphere, and to balance properly the pressures inside and outside the tubes, so that no capillary transpiration may occur.

The air supply for sweeping out the diffusate from the jackets comes from the compressed air supply of the laboratory, and is passed into an empty bottle (23) for settling out impurities, then through 30% caustic soda solution in the very large bottle (24), through the safety bottle (25), through conc. sulfuric acid in a very large bottle (26), and is then blown on the surface of conc. sulfuric acid in the bottle (27). It is then filtered through a foot of glass wool (28) and a foot of absorbent cotton (29), and passes into the distribution line (30). From this it flows through individual stopcocks (31), through flowmeters (32), past sulfuric acid manometers (33), through traps (34) into the jackets of each unit. The traps are used to prevent sulfuric acid from getting into the diffusion units from the manometers or flowmeters. The manometer (35) and that at (12) serve to give the gas pressure in the diffusion line, while those designated as (33) indicate that in the jackets.

Air is passed through each jacket at the rate of 3 liters per minute. During the first diffusion hydrogen chloride passes flowmeter (9) at the rate of 600 cc. per minute, and at this rate  $\frac{1}{30}$  of it arrives at the absorber for the heavy fraction (19) and is collected there. For the second diffusion gas is generated at the same rate, but only four of the units are used. This gives a cut of 20. Third diffusions are run with only the first two units, gas being generated at the rate of 200 cc. per minute, and again a cut of 20 results. The total cut  $30 \times 20 \times 20$ , or 12,000, should, according to the Rayleigh theory, give an atomic weight for the chlorine in the heavy fraction of 35.54, but it is hardly to be expected that an efficiency of 100% in terms of this theory can be obtained, except possibly in a vacuum diffusion, under ideal conditions.

The heavy fraction from each diffusion is neutralized with very pure sodium hydrogen carbonate, and is used in the generator which uses salt (5) for the regeneration of the hydrogen chloride. It is found that the generation from sodium chloride occurs at a more uniform rate if carried out at a temperature of 80° until the charge is nearly spent, when the temperature is rapidly raised to 100°. If the generator at the middle of the run is giving off gas at the rate of over 300 cc. per minute, the salt cake will adhere to the bottom of the flask, until enough sulfuric acid has been run in to float it. Just as it comes loose from the bottom of the flask there is a violent evolution of gas. At rates below 300 cc. per minute the cake is gradually wetted throughout with sulfuric acid and the difficulty is avoided.

It is evident that the process of diffusion may be carried out fractionally and this was done. Thus the light fraction from the second diffusion has nearly as high a density as the heavy fraction from the first diffusion, so it is not rejected, but is rediffused, and the heavy fraction which results has nearly as high a density as that of the original second diffusion.

### Method of Analysis and Calculation of Results.

In order to be able to determine the effects of the successive diffusions it is important to develop a method of determining with considerable precision the change of atomic weight produced. It was found that such

a method could be devised easily provided a simple and seemingly accurate hypothesis is adopted as its basis. This is that isotopes have so nearly the same atomic volumes and the same chemical properties, that no error of sufficient magnitude to affect the analyses will be introduced if it is assumed that they are exactly alike in these respects. That the isotopes of lead have the same volume within the limits of the experimental error has been shown by Soddy<sup>11</sup> and by Richards<sup>12</sup> and that their identity in chemical properties is almost complete is shown by a joint investigation by Gale, Aronberg, and one of the writers,<sup>13</sup> since they found that the difference in the wave length of the line  $\lambda 4058$  caused by a difference of about 0.9 in the atomic weight, was only one-millionth of the wave length. The difference in chemical properties between these isotopes may be expected to be very small. This discovery has been confirmed by Merton.<sup>11</sup> However, even though this hypothesis is used as a basis for calculation, the proof that a *separation* of the two isotopes of chlorine has been made is *entirely independent* of the assumption, since no differences of atomic volume could be detected unless a separation had first been effected.

The simplest method for determining the increase of atomic weight was thought to be the determination of the densities of specimens of highly purified ordinary hydrochloric acid, and a comparison with these of the density of a specimen of acid produced by diffusion. This will be termed the isotopic acid, and the plan was to fix the molecular concentrations of these two acids as determined by titration, at the same value, and to compare the weights of hydrogen chloride which they contain. It is evident that the weight of the isotopic acid should be greater than that of the ordinary or "comparison" acid, since the present article refers to the heavy fraction. These weights are in the same ratio as the formula weights of hydrogen chloride in the two solutions, so

$$\text{and} \quad M_i = 36.468 \cdot W_i/W_c \quad (13)$$

$$A_i = M_i - 1.008 \quad (14)$$

$$\text{or} \quad \Delta A = 36.468 \Delta W/W_c. \quad (15)$$

Here  $M_i$  and  $A_i$  are the molecular weight of hydrogen chloride and the atomic weight of chlorine, respectively,  $W_i$  and  $W_c$  are the weights in grams of the hydrogen chloride in the same volumes (e. g., pycnometer full) of the comparison and the isotopic acids, and  $\Delta W$  is the increase in weight which occurs when the isotopic acid is substituted for the comparison acid. Equation 15 gives the most accurate results, since it does not

<sup>11</sup> Soddy, *Nature*, 94, 615 (1915).

<sup>12</sup> Richards, *THIS JOURNAL*, 38, 221 (1916); and "Presidential Address to the American Association for the Advancement of Science," 1918.

<sup>13</sup> Harkins and Aronberg, *Proc. Nat. Acad. Sci.*, 3, 710-15 (1917); *THIS JOURNAL*, 42, 1328-35 (1920); Aronberg, *Astrophys. J.*, 47, 96-103 (1918); Merton, *Proc. Roy. Soc. London*, 96A, 388-95 (1920).

involve an exact knowledge of the weight in solution of either the comparison or the isotopic acid, but only a precise value for the increase in weight. The thermostat should be regulated to  $0.001^\circ$  or better, and the pycnometer should consist of a large spherical bulb with a short but very narrow neck graduated with a very fine line at its narrowest point. Above the neck is a bulb large enough to hold any solution which rises through the neck on account of thermal expansion. This is fitted with a very close fitting ground-glass stopper, and with very fine tubes for filling and emptying. The pycnometer is preferably made of quartz, and the tubes of platinum or hard gold.

While the above procedure is the simpler from the standpoint of the equations involved, it happens that another method is more economical of time and material, so what has actually been done in most of the cases is to adjust the comparison and the isotopic acids to the same density, and to determine the number of molecules of hydrogen chloride, and therefore the number of atoms of chlorine, present by titration. In this case the acid in the pycnometer has a higher molecular concentration when the comparison acid is used. Very accurate density determinations have been made on solutions of very pure ordinary hydrochloric acid by Dull in this laboratory. From his data it may be calculated that the "apparent density" of hydrogen chloride in 5.91 *N* hydrogen chloride is 1.785, in 5.79 *N* it is 1.7852, while in 5.20 *N* it is 1.787, and in 2.315 *N* it is 1.856.

The difference in the titration values of the comparison and the isotopic acids may easily be calculated in the following way for any desired increase in the atomic weight ( $-\Delta A$ ) of chlorine. Calculate the increase of weight which would occur if the comparison acid in the pycnometer were to be replaced by isotopic acid of the same titration value. Then calculate the number of equivalents of hydrogen chloride in the isotopic acid which must be replaced by water of a density 0.997077 (or 0.99604 as weighed by brass weights in air, if the temperature of the thermostat is  $25^\circ$ ) in order to reduce its weight by the above difference. This gives the difference in the titration values of the two solutions when adjusted to the same density, which will be given directly in terms of 0.01 *N* sodium hydroxide solution, since the titration was completed with a base of this concentration, though begun with 1 *N* solution.

$$\Delta T = \frac{V \cdot N \Delta A}{1000 \cdot M_c} \cdot \frac{d\text{HCl}}{d\text{HCl} - d\text{H}_2\text{O}} \cdot \frac{1}{10^{-5}} \quad (16)$$

$$\text{or} \quad \Delta A = 100 \cdot \Delta T \cdot \frac{d\text{HCl} - d\text{H}_2\text{O}}{d\text{HCl}} \cdot \frac{M_c}{V \cdot N} \quad (17)$$

Here the symbols have the same meaning as before, except that the following new ones are employed:  $M_c$  is the equivalent weight of hydrogen chloride in the comparison acid, and equals 36.468 in the present experi-

ments;  $N$  is the normality of the comparison acid;  $d\text{HCl}$  is the apparent density of hydrogen chloride in the comparison acid;  $d\text{H}_2\text{O}$  is the density of water at the same temperature;  $\Delta T$  is the difference in grams of  $1/100$  weight normal sodium hydroxide between the pycnometer full of the two acids;  $10^{-5}$  is the number of equivalents of sodium hydroxide in 1 cc. of 0.01  $N$  base.  $V$  is the volume of pycnometer in cc. If  $V$  cc. is titrated, the right hand side of the Equation (17) for  $\Delta A$  should evidently be multiplied by  $V/v$ .

Let  $T'_c$  and  $T'_i$  represent the titration values of the comparison and isotopic solutions in terms of normal solutions, then it is evident that Equation 17 may be given the following form.

$$\Delta A = \left( \frac{T'_c}{T'_i} - 1 \right) \frac{d\text{HCl} - d\text{H}_2\text{O}}{d\text{HCl}} \cdot M_c \quad (18)$$

**Method of Adjusting the Densities of the Isotopic and Comparison Acids.**—After a preliminary determination of the densities of the two solutions, the concentration of the solution was read from a graph giving concentrations in terms of the density of ordinary pure hydrogen chloride, and from these values the amount of water necessary to decrease the concentration of the more concentrated solution to that of the more dilute was calculated. This first adjustment brought the densities of the solutions sufficiently close so that a difference of 5 or 6 mg. was all that remained for a volume equal to that of the pycnometer.

A second dilution was made by adding water up to the exact amount called for by the equation  $(d_1 d_2 - d_2) \cdot W_w = W_s (d_2 d_1)$ , where  $d_1$  is the smaller, and  $d_2$  the larger density,  $W_w$  is the weight of water to be added to the weight  $W_s$  of the more dense solution in order to make the densities the same. This equation is not exact, since it takes no account of the volume change produced in adding water to approximately 6  $N$  acid, so it does not bring the two weights closer together than 0.6 mg. An exact equation could easily be developed, but even with the form used only 0.2 g. of water needed to be added to 75 g. of solution in the third dilution.

**Error of Filling.**—The pycnometer could be filled repeatedly with a *maximum* variation of 0.0012%, while the usual error was considerably less. The thermostat was constant to within less than 0.001°.

**Method of Titration.**—First a series of indicator standards was made up in 125cc. tightly glass-stoppered Erlenmeyer flasks.<sup>14</sup> In each of these was put the same volume of conductivity water and the same amount of methyl orange as was used in the titrations. To these were added in order 0, 2, 4, and 6 drops of 0.01  $N$  hydrochloric acid. The titrations

<sup>14</sup> Flasks with very narrow necks will be used for all future work, so that the evaporation may be decreased.

were ended at a color between that in the 2-drop and the 4-drop flasks, and in good daylight the effect of one drop of 0.01 *N* base could be readily detected. A 1 *N* solution of sodium hydroxide was used to carry the titration to within one drop of the end-point, when it was finished with 0.01 *N* solution of the same base. Weight burets of 60 g. capacity were used and these were weighed on a balance sensitive to 0.02 mg. It was found that the use of a heavy "vacuum" stopcock grease completely stopped all loss of weight of the burets due to evaporation of the solutions through the ground-glass stopcocks.

The samples for titration were weighed by measuring 5 cc. of the 6 *N* solution, dropping it into the flask, and then determining the weight on the same balance as that used for the pycnometer. The ground-glass stoppers in the sample flasks were kept dry during the whole determination.

**Purification of Acid.**—The acid used in the analyses as the reference or comparison acid was the light fraction from the first diffusion. A calculation showed that its atomic weight could not have been changed sufficiently to be detectable, and the process used would result in a considerable purification. The acid was treated with potassium permanganate and boiled to expel any iodine, bromine, or chlorine liberated, and was then distilled, rejecting the first third and the last one-fourth.

The isotopic acid was purified in several ways. As has been stated it was formed by the action of very pure sulfuric upon *c. p.* hydrochloric acid. The gas came in contact with only carefully cleaned and dried glass and porous porcelain, and was absorbed in conductivity water. After the second diffusion the salt formed by neutralizing the acid by very pure sodium hydrogen carbonate was recrystallized three times from pure water and was very thoroughly drained and washed with pure water each time. The mother liquor from these crystallizations showed no trace of iodine by the use of a test which would detect one part of iodine as iodide in twenty thousand parts of sodium chloride, as determined by repeated tests. This test consisted in the use of nitrosyl sulfuric acid and carbon disulfide with the proper precautions. Neither could bromine be detected in these mother liquors, but we did not rely upon this fact to insure the absence of bromine. In addition to these three crystallizations, the acid, after the third diffusion was treated with potassium permanganate and distilled using exactly the method employed with the comparison acid, except that the first and last fourths were rejected and the middle half was saved. Additional purifications were made by precipitation of sodium chloride from aqueous solution by the addition of isotopic hydrogen chloride. The sodium hydroxide used in the analyses gave no test for bromine. It was converted into sodium chloride and recrystallized, and the mother

liquor again gave no test for bromine. However, after the sodium hydroxide was added to any sample the latter was always purified carefully.

### Results.

In January, 1920, Mr. C. E. Broeker had produced about 5 g. of hydrogen chloride which was the heavy fraction given by a cut of about 8000. Shortly afterward this was increased to about 20 g. with nearly as large a cut. However, the analyses made in January by Harkins and Broeker used nothing but the original sample. The purification of the acid was made by recrystallization of sodium chloride. In purifying most of the operations are carried out before the sample has been reduced to such a small mass, but at least one purification is always carried out with the final residue. The titration values indicated increases of atomic weight of 0.052, 0.059, 0.057, 0.055, and 0.053 units of atomic weight. A second series of analyses on another sample, gave slightly higher values.

Mr. Broeker's work was interrupted by illness in April, 1920, but on account of his unusual enthusiasm and energy he continued to work for two weeks after his illness began. Since just at this time he adopted a new system of labeling, and his illness took an unexpected turn for the worse and finally resulted in his death, it happened that his records were not completed, and this resulted in some uncertainty in identifying his samples. For this reason, and for the additional purpose of demonstrating that the separation could be carried out by the use of an independent apparatus, and by using different materials, an entirely independent diffusion was started. The hydrogen chloride obtained in the present series of diffusions will be added, in the form of sodium chloride, to the sodium chloride obtained by him, as soon as the atomic weight has increased by the amount given above.

It should be realized that in work of this kind it is not merely the increase in atomic weight which counts, but also the amount of material which is obtained, since the future progress of the work, and also the extent to which the material can be purified, depends largely upon the amount of material available. While the rise in atomic weight obtained in the independent series of diffusions carried out this year, is not large, it seems to be definite, and of the order of magnitude to be expected from the earlier results given above, so a report of progress will be given.

**Analysis of the Purified Third Diffusion Residue (Cut = 12,000).—**In order that the magnitude of the errors involved may be realized the actual data for some of the analyses will be presented. First the reference acid and the isotopic acid were adjusted to practically the same density in a Harkins' pycnometer of about 22cc. volume. The weights were as follows:



## ANALYSES.

	First Series.		Second Series (after another distillation).	
	Weight <i>in vacuo</i> of pycnometer plus.			
	Reference acid.	Isotopic acid. ( $t=25^{\circ}\pm 0.0005^{\circ}$ )	Reference acid.	Isotopic acid.
1.	37.2533	37.2530	37.2100	37.2095
2.	37.2535	37.2527	37.2100	37.2098
	<hr/>	<hr/>	<hr/>	<hr/>
Av.	37.2534	37.25285	37.2100	37.20965
Diff.	0.00055 g. = 0.00148%		0.00045 g. = 0.00121%	

TABLE II.

## DATA ON THE ATOMIC WEIGHT DETERMINATIONS.

Note that the two columns on the left of the table refer to one set of analyses, the two on the right to a second series.

No. of mols. of HCl in 100 g. of sol.; from density.	First Series. $N = 5.91$ .	Second Series. $N = 5.79$ .
Density of Isotopic Acid.	1.10195	1.00983

Bar. Pressure = 748.4 mm. ( $h = 7.17$ )<sup>a</sup> to 746.5 mm.  
( $h = 10.4$ ).  $t = 24^{\circ}$  to  $26^{\circ}$ .

Wt. of pycnometer of water. 35.0350  
" " " 13.2765

DATA FOR THE TITRATION OF THE REFERENCE AND ISOTOPIC ACIDS.<sup>b</sup>

	First Series.	NaOH used per 5 g. of acid.	Second Series.
26.2613	26.1970	25.7887	25.7173
26.2669	26.2004	25.7848	25.7188
			25.7120
	<hr/>	<hr/>	<hr/>
Av. 26.2641	26.1987	25.7867	25.7160
Diff. (g. of 0.01 <i>N</i> NaOH)	6.54		7.07

## After standing for one day.

26.2630	26.2030	25.7755	25.7094
26.2673	26.2069	25.7745	25.7064
	26.2030	25.7752	
	<hr/>	<hr/>	<hr/>
Av. 26.2651	26.2043	25.7751	25.7079
Diff. (g. of 0.01 <i>N</i> NaOH)	6.08		6.72

## After standing for two days.

		25.7695	25.7045
		25.7671	25.7002
		<hr/>	<hr/>
	Av.	25.7688	25.7023
Diff. (g. of 0.01 <i>N</i> NaOH)			6.65

<sup>a</sup> and <sup>b</sup>—For footnotes see next page.

Increase of Atomic Weight.						
	First Series.			Second Series.		
	Uncorr.	Correction for density.	At. wt. increase	Uncorr.	Correction for density.	At. wt. increase.
1st. set.	0.0356	-0.0018	0.0338	0.0393	0.0016	0.0377
2nd. set.	0.0331	-0.0017	0.0312	0.0374	0.0015	0.0359
3rd. set.				0.0370	0.0016	0.0354
Av. increase in at. wt.			0.0325			0.0363
Average of Series 1 and 2			0.0344			

100 g. of chlorine obtained of atomic weight 35.494.

<sup>a</sup> The absolute humidity in mm. of mercury is represented by *h*.

<sup>b</sup> The weights of base and acid used in these titrations are reduced to the same barometric pressure and the same humidity for each series.

The corrections of about 0.0018 for the results of the first, and of 0.0016 for the results of the second series were calculated from the density differences by means of the same equation as was used for the calculation of the results of the titrations.

The difference between the averages of the atomic weights for the first and second series of analyses is 0.0038 units of atomic weight which is very near the possible error in the atomic weight of chlorine according to Richards. While the data given indicate that the comparison method described is a very accurate one for the determination of the atomic weight of an isotope of chlorine, our experience has shown that its precision may be increased, provided as large quantities of acid are available, by the observance of certain precautions which may be introduced. The atomic weight of the chlorine produced by diffusion by the writers is very close to 35.494, while that obtained by Harkins and Broecker was 35.515. However, the amount of material produced by the present work is very much greater, since a few days more of diffusion will give about 100 g. of acid with this atomic weight for the chlorine. Since the efficiency of the process as conducted has not proved to be very high in terms of the Rayleigh diffusion theory, it is planned to conduct the rest of the diffusions upon the smaller portions now on hand, by a vacuum system of diffusion, which should give a high efficiency. The apparatus which is to be used will be described in the next report, and will be similar in many respects to that developed in this laboratory by Dr. Turner for the diffusion of chlorine. Since the amounts of material to be handled are now greatly reduced a further increase of from 0.05 to 0.1 units in addition to that already secured should be obtained quite rapidly, but the rapidity of increase will be dependent upon the amount of the material secured, since a small increase with a large yield of material may be more difficult to secure than a larger increase on a small amount of material.

**Repurified Fourth Diffusion Residue** (Cut = 240,000).<sup>15</sup>—The hydrochloric acid obtained from the third diffusion had been converted largely into sodium chloride in the titrations on the third diffusion residue, so the remaining acid was neutralized with sodium hydrogen carbonate. The salt thus obtained was converted into hydrogen chloride, and again diffused. The hydrochloric acid thus obtained was distilled fractionally, after heating with potassium permanganate. The middle portion was used for the analyses reported below.

## ANALYSES.

	Weight <i>in vacuo</i> of pycnometer plus Reference acid. (t, 25° + 0.0005).		Isotopic acid.
1.	36.4461		36.4465
2.	36.4460		36.4465
Av.	36.44605	Diff. 0.00045	36.4465
No. mols. in 1000 g. solution from density.			Density of isotopic acid.
<i>N</i> = 5.22			<i>d</i> <sub>25</sub> = 1.08868
Barometric pressure = 737 to 739 mm. Absolute humidity = 7.6 to 7.05 mm. Temperature = 24 to 26°.			

Data for the Titration of the Reference and Isotopic Acids.  
(All weights corrected to 737 mm. and *h* = 7.6.)

*N* NaOH per 5 g. of acid.

Reference acid.	Isotopic acid.
First Day.	
G.	G.
23.3430	23.2898
23.3456	23.2870
23.3443	23.2884
Diff. 5.59 g. of 0.01 <i>N</i> NaOH.	
Second Day.	
23.3359	23.2793
23.3401	23.2785
23.3369	23.2755
23.3376	23.2778

Diff. 5.98 g. of 0.01 *N* NaOH.

Increase in Atomic Weight above 35.46.

	Uncorr.	Correction for density.	Atomic weight increase.
1st. day's determinations	0.0346	Add. 0.0017	0.0363
2nd. day's determinations	0.0370	0.0017	0.0387
Av.			0.0375

Nine g. of chlorine of atomic weight 35.498 was obtained in this diffusion. The fourth diffusion was not so efficient as the first three, since the

<sup>15</sup> Report added to paper on May 16, 1921. Determinations by Anson Hayes and S. K. Allison.

apparatus is better designed for larger samples, and in this diffusion the gas passed through only a short length of porous tube of large diameter.

### Result of Additional Purifications.<sup>16</sup>

As has been stated, all of the acid used in this series of determinations was purified after the second diffusion by conversion into sodium chloride through neutralization with very pure sodium hydrogen carbonate, and by three successive fractional crystallizations from pure water. The highly concentrated *mother liquor* from all of these crystallizations, after removing a part of the salt content, gave no test for iodine or bromine. The hydrochloric acid obtained from this salt was, nevertheless, heated with potassium permanganate, and fractionally distilled.

In order to remove all possible doubt in regard to the presence of such impurities, it seemed advisable to make still further purifications. However, this could not be done successfully, using the methods developed for this work, on the 9g. sample of the fourth diffusion residue, since the purification involves the rejection of the greater part of the acid used. The sample was therefore obtained largely by diffusing the *light* fraction from the third diffusion, and adding the considerable quantity of acid thus obtained to the fourth diffusion residue. Since the fourth diffusion had not proved very efficient, the sample thus obtained should have an atomic weight not far from that obtained in the third diffusion residue.

The acid obtained in this way was heated with potassium permanganate and distilled fractionally. The middle portion was neutralized with very pure sodium hydrogen carbonate. Part of the salt thus obtained was then dissolved in 35 cc. of conductivity water, and precipitated by passing in hydrogen chloride generated from the remainder of the isotopic sodium chloride. This purified salt after the hydrochloric acid had been drained off thoroughly was again separated into two portions, and the process was repeated. The apparatus used was wholly of glass.

The 9 g. of sodium chloride thus obtained was carefully separated from the considerable amount of liquid, and the acid still remaining on the salt was driven off by heating in platinum to 300°. The salt was again converted into hydrochloric acid, and was then distilled fractionally. The distillate was again redistilled, and the resulting isotopic acid used in the determinations.

The comparison acid used was subjected to exactly the same set of purifications and treatment using the same apparatus and the same materials, the only difference being that it had not been subjected to the diffusion process. The density determinations and the analyses are given herewith.

<sup>16</sup> Atomic weight determination by Anson Hayes and S. K. Allison. Report added June 9, 1921.

## ANALYSES.

	Reference Acid.	Weight <i>in vacuo</i> of pycnometer plus ( $t = 25^{\circ} \pm 0.0005$ ).	Isotopic Acid.
1.	50.8133		50.8134
2.	50.8136		50.8134
	50.81345		50.8134
	Diff. 0.00005 g.		
	No. of mols in 1000 g. from density. $N$ 2.315		Density of isotopic acid. $d = 1.037855$
	Barometric pressure 754 mm. ( $h = 9.82$ mm.), $t = 22.4^{\circ}$ in balance.		
	Data for the Titration of the Reference and Isotopic Acids. (All weights corrected to 754 mm. and $h = 9.82$ mm.) $N$ NaOH per 10 g. of acid.		
	Reference Acid. G.		Isotopic Acid. G.
	19.6369		
	19.6363		19.5940
	19.6399		
	19.6377		
	Diff. = 4.37 cc. of 0.01 $N$ NaOH.		
	Increase in atomic weight above 45.46		0.0318
	Atomic Weight = 35.4918		

While the above results are all that were obtained under the best conditions on this particular sample, since the other samples were of necessity allowed to stand overnight, two additional titrations of the isotope were then obtained as follows: 19.5974, and 19.6001 g. of  $N$  NaOH to titrate 10 g. of isotopic acid. These confirmed the result obtained above as to its general magnitude, but gave a determination which was slightly more in error. It had been found that under the conditions under which these samples stood, the titration value is very slightly increased, so the atomic weight obtained, from these two titrations, 35.4886, is probably too low. The atomic weight determination for this series is slightly less accurate than for the three preceding series, as the amount of material used was less.

## Summary.

1. A definite increase in the atomic weight of chlorine has been obtained in experiments conducted in this laboratory by the diffusion of hydrogen chloride at atmospheric pressure. The increase in atomic weight amounts in different experiments to from slightly less than to considerably more than one part in a thousand (1 in 645). The amount of separation obtained is in a certain sense considerably more than might be supposed from this figure, since a considerable amount of this isotopic acid has been produced. This seems to be the first separation of isotopes reported from which there is any definite evidence.

2. The separation of isotopes by diffusion is discussed in terms of the Rayleigh diffusion equation, which applies to a diffusion into a vacuum. It is indicated that for a high efficiency the pressure of the gas on both sides of the diffusion wall should be low, first in order to secure good mixing, and second to insure that the passage through the porous partition shall be entirely molecular. Since the large amounts of acid used in the preliminary diffusions have now been largely reduced, the further work in this laboratory will be carried out at low pressures, and with porous material in which the pores are very small.

3. A method which is at the same time very precise and very rapid has been devised for the determination of the atomic weight of any isotopic form of chlorine.

4. It is found that in the separation of isotopes the percentages present of the different isotopes are as important factors as the atomic weight differences. Thus, contrary to what has been supposed, it is shown, even aside from the greater difficulties involved in obtaining and handling neon, that it is easier in terms of the cut necessary to produce a small increase in the atomic weight of chlorine (of the magnitude of 0.05 units) than to produce the same increase in the atomic weight of neon.

5. In January, 1920, Harkins and Broeker had separated 5 g. of isotopic chlorine (in the form of hydrogen chloride) of an atomic weight 35.515. Preliminary notices of this separation were published in the February, 1920, number of the *Physical Review*, in *Science*, and in *Nature*. The present research was begun in order to confirm the earlier work, in June 1920, and has thus far used none of the material left by Mr. Broeker at the time of his death in April 1920. An apparatus of higher capacity, but somewhat lower percentage efficiency, has been used. Nine g. of chlorine of atomic weight 35.498, and 90 g. of atomic weight 35.494, have been obtained, the atomic weight results having been determined upon very highly purified material. In addition to this considerable isotopic chlorine of lower atomic weight has been obtained, about 400 g., whose atomic weight has not been determined, but should be more than 0.02 units higher, and 4 kg., whose atomic weight should be more than 0.01 unit higher, than for normal chlorine, judging from the efficiency of the whole process. Dr. W. D. Turner prepared several kg. of this last grade in the summer of 1918, and about 20 g. of much more highly diffused chlorine in 1916-7, but the atomic weight work was left incomplete on account of the war. A notice of the beginning of this work was published in THIS JOURNAL in January, 1916. In 1915, definite evidence based upon atomic weight relations was presented by one of the writers that chlorine consists of isotopes. An important feature of the present investigation is that it was begun four years before any entirely direct experiments had proved the existence of isotopes in chlorine, and a

notice of the separation was published only two months after Aston's preliminary notice in regard to their existence.

The writers wish to express their indebtedness to the C. M. Warren Fund of the American Academy of Arts and Sciences for a grant of five hundred dollars to be used in carrying on the present investigation. A part of this has been used in the purchase of an analytical balance sensitive (for a  $1/2$  mm. deflection) to  $1/100$  mg. to be used in weighing small samples of higher or lower atomic weight. Thanks are also due to the Wolcott Gibbs Fund of the National Academy of Sciences for a similar grant to be used in determining the effects of radiation and high temperatures upon the stability of the nucleus of the atom, and also for positive ray work upon isotopes. We wish to thank the Grasselli Chemical Company of Cleveland, Ohio, and the Mallinckrodt Chemical Company of St. Louis for gifts of considerable amounts of hydrochloric and sulfuric acids; the Jaques Mfg. Co. for a barrel of sodium hydrogen carbonate which proved to be purer than the "analyzed" material previously purchased; Dr. F. L. Dunlap for his assistance in securing material; T. H. Liggett and S. K. Allison for assistance in the experimental work; and the Bureau of Standards and the Coors Porcelain Company for the preparation of tubes of different porosities.

Diffusions on the light fraction were carried out by C. E. Broeker in the year 1919-20, and the results of this work will be reported in a later paper. It is hoped that funds for the construction of a centrifugal machine may be secured, as it seems probable that the centrifugal method, or at least some method other than those of diffusion, thermal diffusion, or vaporization at low pressures, must be used if a separation of any considerable magnitude is to be obtained without the expenditure of an unreasonable amount of effort.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 369.]  
**COMPOUND FORMATION AND VISCOSITY IN SOLUTIONS  
OF THE TYPES ACID : ESTER, ACID : KETONE, AND ACID : ACID.**

BY JAMES KENDALL AND ELIZABETH BRAKELEY.

Received May 16, 1921.

In a recent article<sup>1</sup> the complete specific conductivity-composition curves for a number of systems of the above types have been presented, and their significance with respect to the fundamental relationship between compound formation and ionization in solutions, as postulated in previous papers,<sup>2,3</sup> critically examined. The point was made clear in the discussion, however, that for a strict comparison of ionization equilibria throughout the different systems a knowledge of other variables was necessary. Among these variables the first in importance is viscosity.

In the present communication the viscosity—composition curves for certain of the above systems are given, not so much with the idea of making immediate and final corrections in the corresponding specific conductivity curves as with the hope of obtaining additional and confirmatory information regarding the relative extent and stability of compound formation between the components in such systems. When progress in other lines has been made, the results here obtained will of course ultimately be of service in making exact corrections upon the conductivity data. The present impossibility of such a procedure, however, is discussed in a later section.

### Experimental.

The following systems have been investigated: (a) *acid:ester systems*, trichloro-acetic acid and acetic acid with ethyl acetate and ethyl benzoate; (b) *acid-ketone systems*, trichloro-acetic acid and acetic acid with acetone and acetophenone; (c) *acid:acid systems*, trichloro-acetic acid with acetic acid.<sup>4</sup>

The same careful methods of purification of the substances employed, described in earlier articles<sup>5,6</sup> were followed, and materials of the same high order of purity, as evidenced by suitable physical constants in each case, were obtained throughout. The apparatus used for the determination of viscosities was of the Bingham type.<sup>6,7</sup> The experimental procedure was essentially as given in previous work,<sup>8</sup> the only new feature

<sup>1</sup> Kendall and Gross, *THIS JOURNAL*, **43**, 1426 (1921).

<sup>2</sup> Kendall and Booge, *ibid.*, **39**, 2323 (1917).

<sup>3</sup> Kendall and Gross, *ibid.*, **43**, 1416 (1921).

<sup>4</sup> Other examples of this type (and of its extension into the type: acid-base) have been taken up by previous investigators. The results obtained by them are utilized in the discussion below.

<sup>5</sup> Kendall and Wright, *THIS JOURNAL*, **42**, 1776 (1920).

<sup>6</sup> Bingham, *J. Ind. Eng. Chem.*, **6**, 233 (1914).

<sup>7</sup> Bingham, Schlesinger and Coleman, *THIS JOURNAL*, **38**, 27 (1916).

<sup>8</sup> Kendall and Monroe, *ibid.*, **39**, 1787 (1917).



presented being the necessity of adopting particular precautions for the protection of the materials employed against water vapor, the hygroscopic character of certain of the substances used (*e. g.*, trichloro-acetic acid<sup>9</sup>) being very pronounced.

TABLE I.  
PROPERTIES OF PURE COMPONENTS.

Liquid.	Freezing pt. °C.	Boiling pt. (760 mm.) °C.	Density. 25°/4°.	Viscosity. 25°.	Spec. conductivity. (mhos) 25°.
Ethyl acetate	....	77.1 ± 0.05	0.8948	0.004236	1 × 10 <sup>-9</sup>
Ethyl benzoate <sup>10</sup>	....	212.9 ± 0.1	1.0458	0.01982	1 × 10 <sup>-9</sup>
Acetone <sup>11</sup>	....	....	0.7872	0.003065	6 × 10 <sup>-8</sup>
Acetophenone	....	202.3 ± 0.1	1.0263	0.01681	5.5 × 10 <sup>-8</sup>
Acetic acid <sup>12</sup>	16.57 ± 0.05	117.8 ± 0.1	1.0499	0.01121	2.4 × 10 <sup>-8</sup>
Trichloro-acetic acid <sup>13</sup>	59.2	....	(1.62)	(0.0683)	(3 × 10 <sup>-9</sup> )

The viscosity results obtained for the various systems at 25° are presented in the tables below. Density data are also appended, to enable transformation of the results from molecular percentages to volume percentages to be made if desired. With the Bingham viscometer, very accurate density determinations are not necessary,<sup>14</sup> and the values given are not to be relied upon beyond the third decimal place. The mixtures investigated being essentially non-ideal, linearity in the density-volume composition curve is not to be expected. In some of the systems, considerable heat effects were evident on admixture.

TABLE II.  
TRICHLORO-ACETIC ACID : ETHYL ACETATE.

Mol. % acid.	d <sub>4</sub> <sup>25</sup> .	Viscosity.
0.00	0.8948	0.004236
11.18	0.9972	0.005878
18.40	1.045	0.007309
28.07	1.123	0.01001
38.46	1.202	0.01449

TABLE III.  
ACETIC ACID : ETHYL ACETATE.

Mol. % acid.	d <sub>4</sub> <sup>25</sup> .	Viscosity.
0.00	0.8948	0.004236
10.49	0.9092	0.004590
20.70	0.9211	0.004949
30.37	0.9308	0.005331
39.90	0.9417	0.005762

<sup>9</sup> Work with this substance was confined to cold, dry days.

<sup>10</sup> The density here obtained is slightly greater than that given by Kendall and Wright (*Ref. 5*); the viscosity is slightly less, but practically identical with the former value of Kendall and Monroe. The boiling-point recorded in Kendall and Wright's article (*p. 778*) is in error, the value for a preliminary sample having been accidentally substituted.

<sup>11</sup> Jones and Mahin (*Am. Chem. J.*, 41, 440 (1909)) quote a much higher viscosity for acetone. The result here given, however, is very close to the interpolated value of Thorpe and Rodger (*Phil. Trans.*, 185A, 397 (1894)) and to the more recent value of Dunstan and Hilditch (*Z. Elektrochem.*, 18, 186 (1912)).

<sup>12</sup> Dunstan (*Z. physik. Chem.*, 51, 732 (1905)) gives a higher viscosity value, but the present result is again in good agreement with Thorpe and Rodger's data.

<sup>13</sup> The values given are extrapolated from measurements at higher temperatures, as described later.

<sup>14</sup> The density enters into the working formula only in a correction factor (approximately 1% of the total), hence approximate values are sufficient. In a few cases the figures given are interpolated results.

TABLES II AND III (Continued).

Mol. % acid.	$d_4^{25}$	Viscosity.	% acid.	$d_4^{25}$	Mol. Viscosity.
48.78	1.295	0.02176	49.85	0.9557	0.006289
61.42	1.386	0.03467	59.96	0.9697	0.006890
70.08	1.454	0.04709	69.88	0.9850	0.007668
			80.11	1.0015	0.008590
			87.42	1.0165	0.009430
			100.00	1.0499	0.01121

TABLE IV.

TRICHLORO-ACETIC ACID : ETHYL BENZOATE.

Mol. % acid.	$d_4^{25}$	Viscosity.
0.00	1.0458	0.01982
8.874	1.0864	0.02324
20.96	1.1466	0.02930
31.25	1.1915	0.03711
39.82	1.2413	0.04610
49.07	1.2922	0.05848
57.95	1.3501	0.07068
67.58	1.4027	0.08374

TABLE V.

ACETIC ACID : ETHYL BENZOATE.

Mol. % acid.	$d_4^{25}$	Viscosity.
0.00	1.0458	0.01982
10.41	1.046	0.01948
21.29	1.046	0.01874
30.45	1.047	0.01797
38.82	1.047	0.01727
47.50	1.047	0.01651
58.22	1.048	0.01538
68.26	1.048	0.01446
79.56	1.049	0.01322
91.32	1.049	0.01202
100.00	1.050	0.01121

TABLE VI.

TRICHLORO-ACETIC ACID : ACETONE.

Mol. % acid.	$d_4^{25}$	Viscosity.
0.00	0.7872	0.003065
4.84	0.8541	0.003680
13.16	0.9342	0.004855
25.43	1.073	0.008156
38.26	1.209	0.01433
50.48	1.319	0.02571
59.71	1.400	0.03829
71.75	1.483	0.05808

TABLE VII.

ACETIC ACID : ACETONE.

Mol. % acid.	$d_4^{25}$	Viscosity.
0.00	0.7872	0.003065
9.96	0.8089	0.003496
20.35	0.8351	0.004046
30.25	0.8568	0.004636
40.49	0.8847	0.005350
49.86	0.9064	0.006098
59.73	0.9333	0.006994
69.68	0.9609	0.008026
80.15	0.9907	0.009213
90.37	1.0255	0.01036
100.00	1.0499	0.01121

TABLE VIII.

TRICHLORO-ACETIC ACID : ACETOPHENONE.

Mol. % acid.	$d_4^{25}$	Viscosity.
0.00	1.026	0.01681
8.96	1.076	0.02112
14.00	1.103	0.02402
21.21	1.146	0.02931
29.39	1.192	0.03735
40.90	1.268	0.05540
48.76	1.317	0.07349
57.94	1.376	0.09330
68.15	1.442	0.1115

TABLE IX.

ACETIC ACID : ACETOPHENONE.

Mol. % acid.	$d_4^{25}$	Viscosity.
0.00	1.0263	0.01681
9.98	1.0272	0.017407
21.07	1.0287	0.017536
29.35	1.0300	0.01742
42.53	1.0325	0.01703
48.85	1.0338	0.01668
60.03	1.0365	0.01598
69.98	1.0390	0.01524
80.02	1.0420	0.01420
90.13	1.0453	0.01293
100.00	1.0499	0.01121

TABLE X.

TRICHLORO-ACETIC ACID : ACETIC ACID.

Mol. % $\text{CCl}_3\text{COOH}$ .	$d_4^{25}$ .	Viscosity.
0.00	1.049	0.01121
7.37	1.129	0.01532
17.77	1.223	0.02228
32.09	1.337	0.03362
43.48	1.409	0.04346
52.62	1.457	0.05176
58.53	1.491	0.05859
65.81	1.508	0.06854

## Consideration of Results.

The majority of the systems with trichloro-acetic acid as one component are reproduced in diagram form in Fig. 1; those with acetic acid as one component are shown in Fig. 2.

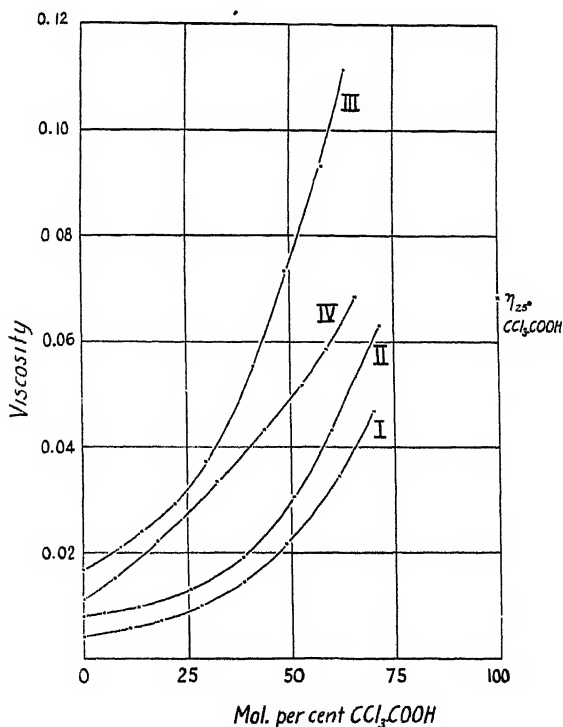


Fig. 1.—Trichloro-acetic acid systems. I. Trichloro-acetic acid:ethyl acetate; II. Trichloro-acetic acid:acetone (subtract 0.005 from viscosity scale); III. Trichloro-acetic acid:acetophenone; IV. Trichloro-acetic acid:acetic acid,

It will be noticed that the trichloro-acetic acid curves are incomplete. This is due to the fact that pure trichloro-acetic acid melts at  $59.4^{\circ}$ ; consequently solutions containing more than 70 mol. % (approximately) of trichloro-acetic acid begin to solidify at temperatures above  $25^{\circ}$ . In a few cases slightly supercooled solutions were successfully investigated at this temperature. With any large excess of acid, however, crystallization during the determinations, stopping up the capillary and rendering all measurements impossible, could not be prevented.

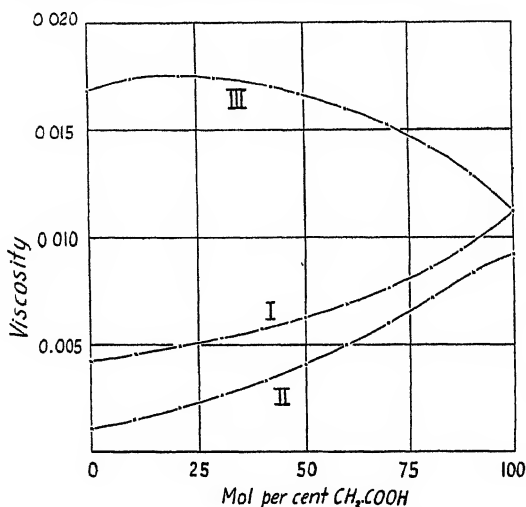


Fig. 2.—Acetic acid systems. I. Acetic acid: ethyl acetate; II. Acetic acid: acetone (add 0.002 to viscosity scale); III. Acetic acid: acetophenone.

An approximate value for the viscosity of pure trichloro-acetic acid at  $25^{\circ}$  was derived by making measurements with an Ostwald viscometer in a small bath at two temperatures above its melting point and extrapolating the results. At  $60^{\circ}$  the density and viscosity were 1.595 and 0.0397 respectively, and at  $70^{\circ}$  they were 1.588 and 0.0315. By linear extrapolation the viscosity at  $25^{\circ}$  is 0.0683; in view of the uncertainty of the extrapolation<sup>15</sup> and the relatively large experimental errors involved in the Ostwald method of measuring viscosity this figure must be regarded as merely indicative.

The position of the point for pure trichloro-acetic acid on the diagram

<sup>15</sup> Viscosity is not, of course, a linear function of temperature, but the various relationships proposed for normal liquids (Batschinski, *Z. physik. Chem.*, 84, 643 (1913); Arrhenius, *Meddel. K. Vetenskapskad. Nobelinst.*, 3, No. 20 (1918)) will certainly not be applicable to an associated liquid such as trichloro-acetic acid. Linear extrapolation is here adopted as the simplest possible procedure and cannot, in view of the shortness of the temperature interval, involve any extreme error.

(Fig. 1), however, makes it evident that the viscosity curves for all systems examined containing this acid as one component exhibit a very sharp maximum in the neighborhood of 80 to 90 mol. % acid. The existence of such a maximum must be ascribed, in each case, to the extensive formation of complex addition compounds of higher viscosity than the pure components. It was at one time common practice<sup>16</sup> to deduce the formulas for such addition compounds from the position of the maximum on the composition axis. The fallacy of such a procedure has been exposed by Findlay<sup>17</sup> and by Denison,<sup>18</sup> who have employed the more logical method of marking the position of maximum deviation from the normal curve rather than the actual maximum point. Unfortunately, in the case of viscosities, we have not yet succeeded in establishing the ideal curve<sup>19</sup> all that we know with certainty is that it is not linear but considerably sagged. We cannot therefore postulate, from examination of the above curves, what compounds are present in the solutions. We are justified, however, in regarding the curves as confirming the fact, already indicated by freezing-point data, that addition compounds are formed in quantity in all cases.

The curves with acetic acid as one component are of a different nature. Only in one system here studied (acetic acid:acetophenone) is a maximum obtained, and even this is exceedingly flat. While we can legitimately draw, from this, the conclusion (also previously indicated by freezing-point data<sup>20,21</sup>) that compound formation is in general much less extensive in systems of esters and ketones with acetic acid than in systems of the same substances with trichloro-acetic acid, yet the absence of a maximum must not be taken to signify that compound formation is entirely absent. Thus the curve for the system acetic acid:acetone is not sagged throughout, but shows a point of inflection; while the curve for the system acetic acid:ethyl benzoate is entirely concave (instead of convex) towards the composition axis. Compounds are evidently present in solution in these cases in quantity sufficient to raise the curves considerably above their normal position, but insufficient to produce an actual maximum. Even in the curve for the system acetic acid:ethyl acetate, which is sagged and apparently ideal throughout, compound formation is undoubtedly a factor, for acetic acid is a typical associated liquid and the addition of a substance entirely inert towards it would normally result in a viscosity curve with a minimum point, due to the progressive disassociation of the acetic acid into less viscous simple molecules as its concentration in the

<sup>16</sup> For references see Walden, *Akrens' Sammlung*, 15, 397 (1910).

<sup>17</sup> Findlay, *Z. physik. Chem.*, 69, 217 (1909).

<sup>18</sup> Denison, *Trans. Faraday Soc.*, 8, 35 (1912).

<sup>19</sup> See Kendall and Monroe, *THIS JOURNAL*, 43, 115 (1921).

<sup>20</sup> Kendall and Booge, *ibid.*, 39, 1712 (1916).

<sup>21</sup> Kendall and Gibbons, *ibid.*, 37, 149 (1915).

solution diminishes.<sup>22</sup> Compound formation, in this case, must approximately counterbalance such disassociation. In the other systems, for the same reason, the true extent of compound formation must be greater than that which is apparent from the shape of the curves (particularly in a case such as acetic acid: acetone, where *both* components of the system are highly associated liquids), owing to the obscuring effect of the disassociation factor.

**Systems of the Type Acid:Acid and Acid:Base.**—The one system of the type acid:acid here examined (trichloro-acetic acid:acetic acid) gives a sharp maximum on the viscosity curve (see Fig. 1), although at 25° this maximum cannot be experimentally realized owing to its proximity to the trichloro-acetic acid side of the diagram. The viscosity results thus confirm the extensive formation of addition compounds between the two acids of widely divergent acidic strengths previously suggested by freezing-point depression measurements.<sup>23</sup> It is of importance to note that the viscosity curve for the system acetic acid:sulfuric acid<sup>24</sup> also shows a maximum. In this case the existence of an equimolecular compound ( $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{SO}_4$ ), with melting point  $-2.5^\circ$ , has been directly established by examination of the freezing-point curve.<sup>25</sup> With acids of similar acidic strength, however, (*e. g.*, formic acid,<sup>26</sup> propionic acid) acetic acid gives a typically sagged curve, indicating that compound formation is practically non-existent.

When we consider acetic acid with bases, increasing diversity again involves increasing compound formation and the maximum reappears. Thus acetic acid:formamide<sup>27</sup> and acetic acid:water<sup>28</sup> both show curves with comparatively flat maxima. With a still stronger base, (acetic acid:aniline<sup>29</sup>) the maximum becomes very sharp, flattening out only at high temperatures.

Many other examples of the type acid:base, of similar character, have been investigated by previous workers. It will suffice here to mention the curve for the system sulfuric acid:water<sup>30</sup> (which gives a very sharp maximum corresponding to the very stable compound  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ) and the recent work of Bramley<sup>31</sup> on systems of the type phenol: aniline.

<sup>22</sup> Kendall and Monroe, *THIS JOURNAL*, 43, 122 (1921).

<sup>23</sup> Kendall, *ibid.*, 36, 1722 (1914).

<sup>24</sup> Drucker and Kassel, *Z. physik. Chem.*, 76, 363 (1911).

<sup>25</sup> Unpublished work of Kendall and Davis.

<sup>26</sup> Herz, *Z. anorg. Chem.*, 104, 51 (1918).

<sup>27</sup> Merry and Turner, *J. Chem. Soc.*, 105, 758 (1914).

<sup>28</sup> Dunstan and Thole, *ibid.*, 95, 1560 (1909).

<sup>29</sup> Faust, *Z. physik. Chem.*, 79, 106 (1912).

<sup>30</sup> Dunstan and Wilson, *J. Chem. Soc.*, 91, 83 (1907).

<sup>31</sup> Bramley, *ibid.*, 109, 10, 434 (1916).

**Application of a Viscosity Correction to Conductivity Data.**—Walden<sup>32</sup> has shown that for a fixed solute (tetra-ethylammonium iodide) in a series of very divergent solvents the product of  $\Lambda_{\infty}$  and  $\eta$  is practically a constant; in other words, the mobilities of the ions are inversely proportional to the viscosity of the medium. If Walden's rule could be directly extended to the systems investigated in this paper, we could at once transform the specific conductivities as determined by Kendall and Gross to relative ionic concentrations by multiplying throughout by the viscosity of each particular solution. Considerable doubt has been cast by subsequent workers<sup>33</sup> in this field, however, upon the general validity of Walden's rule, and the conditions here existent are so different from those in the solutions examined by Walden that we are compelled to hesitate in making this step until more definite advances have been made, lest by attempting to compare our results on a false basis we arrive at entirely unjustified conclusions.

Walden worked with a single solute only<sup>34</sup> (and that a salt, as recent work indicates,<sup>35</sup> of exceptional character) at very low concentrations. In any particular solvent, therefore, the degree of solvation of the ions would not appreciably vary. In the present work, we are dealing with solutions with compositions ranging all the way from pure component A to pure component B, and the average ionic complexity will undoubtedly change very significantly with composition.<sup>36</sup> In the case of aqueous solutions of salts at moderate concentrations, Green<sup>37</sup> and Washburn<sup>38</sup> have established that a fractional power viscosity correction is more accurate than a linear correction, presumably on account of decreasing hydration of the ions with decreasing water concentration.<sup>39</sup> Here, with a much more extended concentration range, viscosity variations are so enormous (over 1000% in some systems) that the value of the exponent in any fractional power correction would need to be very accurately

<sup>32</sup> Walden, *Z. physik. Chem.*, **55**, 246 (1906).

<sup>33</sup> For example, Fitzgerald has shown that  $\Lambda_{\infty}\eta$  is by no means constant for salts in liquid ammonia, sulfur dioxide and water (*J. Phys. Chem.*, **16**, 645 (1912)). For further references see Kraus, *THIS JOURNAL*, **36**, 35 (1914); Ghosh, *J. Chem. Soc.*, **117**, 1390 (1920).

<sup>34</sup> In an article which has just appeared (*Z. anorg. Chem.*, **113**, 85 (1920)) Walden has tried to extend his rule to other solutes, partly answering and partly admitting the objections made by other investigators.

<sup>35</sup> Ghosh, *J. Chem. Soc.*, **113**, 630 (1918); Walden, *Z. physik. Chem.*, **94**, 295 (1920).

<sup>36</sup> See Kendall and Gross, *THIS JOURNAL*, **43**, 1436 (1921).

<sup>37</sup> Green, *J. Chem. Soc.*, **93**, 2049 (1908).

<sup>38</sup> Washburn, *THIS JOURNAL*, **33**, 1461 (1911).

<sup>39</sup> Similarly Johnston (*ibid.*, **31**, 1010 (1909)) found a fractional power relationship to exist between  $\Lambda_{\infty}$  and  $\eta$  as temperature is varied. Schlesinger and Coleman, however, in the case of metal formates in formic acid solutions, claim that no viscosity correction at all is to be applied (*ibid.*, **38**, 271 (1916)).

determined to fix the final position of a curve. Since, furthermore, different systems might very conceivably require quite different exponents and would almost certainly give significantly different values for the product  $\Delta_{\infty}\eta$ , any rigorous comparison at this stage is obviously altogether impracticable.

As has been shown above, however, the viscosity results in themselves furnish us with considerable additional information on compound formation in the systems studied, confirming very strongly the rule that compound formation is fundamentally dependent upon diversity in character of the constituent groups of the components, and the data here presented will later, it is hoped, be utilized in making exact and dependable corrections upon the conductivity results of Kendall and Gross.

### Summary.

The viscosity-composition curves for the following systems at 25° have been determined: (1) trichloro-acetic acid:ethyl acetate, (2) acetic acid:ethyl acetate, (3) trichloro-acetic acid:ethyl benzoate, (4) acetic acid:ethyl benzoate, (5) trichloro-acetic acid:acetone, (6) acetic acid:acetone, (7) trichloro-acetic acid:acetophenone, (8) acetic acid:acetophenone, (9) trichloro-acetic acid:acetic acid.

The results obtained indicate extensive compound formation in solutions of the esters and ketones with a strong acid (trichloro-acetic). The same substances with a weak acid (acetic) give viscosity curves which are much less abnormal, although compound formation is still evident. The curve for the system trichloro-acetic acid:acetic acid exhibits considerable compound formation, and an examination of the results of previous workers on systems of the types acid:acid and acid:base shows that this behavior is general, except when the components are of similar acidic strength. The rules formulated in previous articles relating the extent of compound formation with diversity in character of the components are hereby confirmed.

The results here presented may ultimately be employed to place the specific conductivity data obtained by Kendall and Gross for the same systems upon a strictly comparable basis. The difficulties which prevent this step being made immediately have been briefly discussed.



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## THE MEASUREMENT OF DIELECTRIC CONSTANTS.

BY J. F. KING AND W. A. PATRICK.

Received May 19, 1921.

This preliminary paper contains a description of a bridge method for measuring dielectric constants of liquids in which use is made of audion bulbs both as a source of exciting current and as a means of determining the balance point of the bridge. Our interest in the dielectric constant is due to the suspected close relationship that exists between this constant and the solvent power of liquids. That there is a relation between the swelling powers of liquids and their dielectric constants is apparent from a casual review of the experimental data. However, there are many exceptions to the rule and our effort is directed toward the possibility of finding a more general relationship.

Accordingly, we planned first to measure the dielectric constants of a series of liquids and mixtures of the same and also the swelling power, or as it is incorrectly called the "solvent" power, that these exerted upon a certain sample of cellulose nitrate.

Our choice of a suitable method for the measurement of dielectric constant was greatly influenced by the result of a year's work in this field by one of the authors. This work (unpublished) was done in University College, London, together with Professor F. G. Donnan and resulted in the conviction that there is no satisfactory method for the measurement of dielectric constant of liquids possessing a specific conductivity greater than that of conductivity water. In this work the Drude<sup>1</sup> method as well as Schmidt's<sup>2</sup> modification was carefully investigated, using a well constructed apparatus in which special attention was paid to the exciting energy and the end-point detectors. A 30cm. spark induction coil was employed, operated with a mercury break interrupter. This induction coil was connected to a Tesla converter, the energy from which was used to excite the primary circuit of the testing apparatus. Neon tubes were prepared and the most sensitive ones were used in determining the end-point. The results of the experiments with this apparatus showed that neither from the standpoint of precision nor from the standpoint of the ability to measure the dielectric constants of conducting liquids, does this apparatus have the advantages which have been claimed for it over other methods. When liquids that possessed a conductivity only slightly greater than that of conductivity water were used, the minima became very obscure, and furthermore during the measurement a large increase in the temperature of the liquid was observed, indicating that energy

<sup>1</sup> Drude, *Z. physik. Chem.*, 23, 267 (1897).

<sup>2</sup> Schmidt, *ibid.*, 27, 343 (1898).

absorption was taking place. This energy absorption increased with the increase in frequency of the electric wave. This is important from the chemist's viewpoint since it is commonly understood that an increase in the frequency of the electric wave enables one to measure the dielectric constant of a conducting liquid.

Many experiments were made with the well-known bridge method as developed by Nernst.<sup>3</sup> Special attention was given here to the source of alternating current. Electrically driven tuning forks of various frequencies within the telephonic range were used, as well as a variety of other well-known interrupters. The sharpest minima, however, were obtained with a small Wehnelt break. All manner of changes in the apparatus did not develop an arrangement which was especially satisfactory. The principal objection was the lack of precision. The sources of current producing the more symmetrical electric waves gave minima which extended over a large portion of the setting scale.

From a theoretical consideration of the distribution of an alternating current in a Wheatstone bridge, we decided to use as our source of alternating current an apparatus which would furnish a symmetrical wave. This is an important factor in the measurement of dielectric constant for the assurance of a sharp and true minima. Professor Flemming<sup>4</sup> has given it consideration in his statement, "It may be pointed out incidentally that no accurate balance or well defined zero can be obtained unless the electromotive force applied to the bridge has a very true sine wave form. Hence no arrangement such as a buzzer, hummer or current interrupter of any kind can be substituted for the sine curve alternator or for an alternator and a wave filter."

We used a frequency of about 1000 cycles per second since this is within the telephonic range and gives a pitch easy to detect and since there is nothing to be gained by using a higher frequency. The work of one of us cited above showed that there is greater energy absorption at higher frequencies. Flemming has treated this matter theoretically and has shown that greater dissipation of current due to the dielectric occurs at higher frequencies. With a slightly conducting liquid in our cell we have to measure the capacity similar to that of a leaky condenser. Flemming has shown that the energy loss in a poor dielectric due to an alternating current can be divided into two parts, the first due to conductivity which is probably electrolytic in nature and the second to a conductivity which is nearly proportional to the frequency. The first is the regular direct current conductance while the second has been called an alternating current conductance.

In the method worked out by Nernst, the ratio arms of the bridge

<sup>3</sup> Nernst, *Z. physik. Chem.*, **14**, 622 (1894).

<sup>4</sup> Fleming, *Proc. Phys. Soc. London*, [2] **23**, 117 (1911).

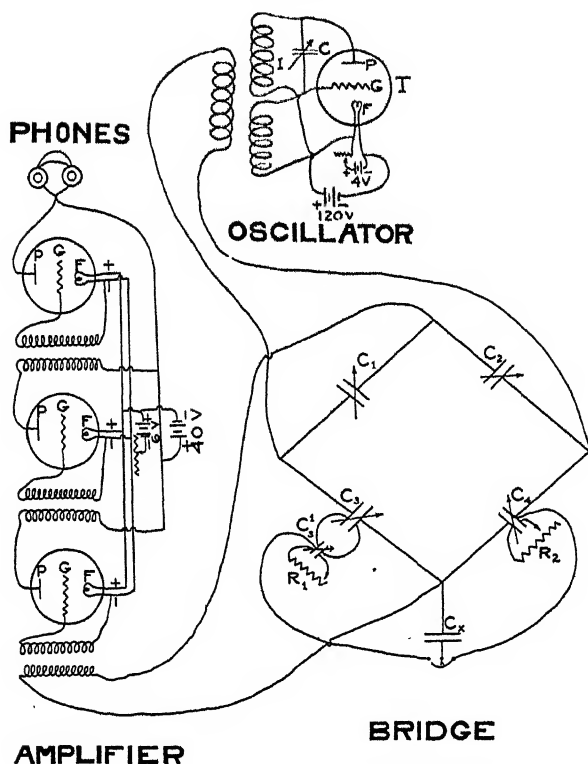
consisted of two resistances and the other arms consisted of an unknown capacity which was balanced by a measuring condenser. In order to make the impedance in the ratio arms of the same magnitude as the impedance in the balancing arms, it was necessary to use very large resistances with the possibility of introducing self-induction into those arms of the bridge. We used air condensers in all four arms. Air condensers are to be desired because of their more constant capacity and the smaller chance for leakage.

Since, with a conducting solution in our dielectric cell condenser, we had to balance a leaky condenser, we used a non-inductive resistance shunted around the measuring condenser in the balancing arm of the bridge. Although Flemming<sup>4</sup> has shown that it is not possible to duplicate a leaky condenser by means of a condenser and a resistance in parallel, we were able to prove that up to a certain limiting value of shunted conductivity it was possible to obtain true values of the capacity of the condenser.

Much attention has been given by conductivity workers and workers on the bridge method for the measurement of dielectrics to the phone used to detect the minima. The minimum current possible in the bridge is determined by the current necessary to excite the phones. This minimum current is still large enough to cause trouble in the matter of heating effects, polarization, etc. A small current is to be desired, but using a small current and one of symmetrical wave form much difficulty is experienced in reaching a minimum. To overcome this difficulty we used the thermo-ionic amplifier of recent development. With this improved apparatus, consisting of a source of alternating current of symmetrical wave form, a symmetrical bridge, each arm of which offered an impedance of the same magnitude, and with an extremely small current flowing through the bridge, the use of which was made possible by the amplifier in connection with the telephones, we hoped for an improvement in the accuracy of our measurements.

The Vreeland oscillator is without doubt the best source of alternating current of sine wave form, but the cost of the Vreeland oscillator led us to turn to the electron tube as our source of current. By an arrangement in which an electron tube, a condenser and an induction coil are connected in a circuit, it is possible to obtain an alternating current of symmetrical wave form. With this arrangement by properly varying the plate voltage, the temperature of the filament, the capacity and the induction, it is possible to obtain different currents varying from a few tenths of a milliamperer or less to 25 amperes and with a frequency varying from  $\frac{1}{2}$  cycle per second to 50 million cycles per second.<sup>5</sup>

<sup>5</sup> Hall and Adams, *THIS JOURNAL*, 41, 1515 (1919).



## DIELECTRIC CONSTANT APPARATUS

We used the "Marconi Vacuum Tube" type V.T.1. In the drawing, T is the vacuum tube, C the condenser, and I the induction coils. The audion plate was charged with 120 volts by dry cells while the filament was heated with a current of 0.7 ampere and 4 volts supplied from lead storage cells. The two induction coils consisted of about 300 turns of No. 32 wire each wound around a laminated iron core. The lead to the bridge was coupled to this with about 50 turns on the secondary coil. At C are two variable Murdock condensers connected in parallel. By adjustment of these condensers we obtained a frequency of about 1000 cycles per second. During the first part of our work we used the laboratory current to charge the plates in the electron tubes both in the amplifier and in the oscillator. Great difficulty was experienced from external noises caused from other electrical apparatus running in the building which tended to obscure the minimum and greatly tried the patience of the operator; but when dry cells were used to supplant the laboratory current the results were most gratifying.

In the construction of the bridge, two variable Murdock air condensers were used in the ratio arms.<sup>5</sup> The condensers had a capacity of about 0.0005 microfarad and the scales were divided into 180 divisions. In any series of measurements these condensers were set and the moving pointer sealed by means of sealing wax. These condensers

<sup>5</sup> These condensers as well as most of the wireless apparatus were purchased from the Wireless Specialty Co. of Boston.

are represented by  $C_1$  and  $C_2$  in the drawing. In the measuring arm of the bridge were the following parts.

1. A variable vernier condenser,  $C_3$  in the drawing, "DeForest" type, with a capacity of 0.0015 microfarad. The scale was divided into 100 divisions. The vernier had a capacity of about 180 degrees per scale division. The pointer on this scale was extended about 75 cm. to an enlarged scale of some 2200 divisions of 1 mm. each, thus enabling us to set the condenser with a much greater precision. In making a measurement, the setting was made on the large scale and then the accuracy of the scale was tested by means of the vernier condenser. The vernier was moved by means of a lever operated from the center of the room. This was done to prevent the introduction of capacity into the bridge from the operator's body. If after making a setting on the large scale, the vernier, by a small movement to the right and to the left, passed through a minimum, we assumed the setting to be correct.

2. Connected in parallel with this measuring condenser was a second Murdock condenser,  $C_3'$ , from which about half of the plates had been removed. The recording pointer of this condenser was also extended to an enlarged scale. It was possible to use the large condenser for changes in dielectric from 2 to about 26 and over and the small condenser for changes from 2 to 7, gaining a 5-fold increase in sensitivity. The vernier setting-lever was used for testing the setting of the minimum when either condenser was used. When  $C_3$  was used,  $C_3'$  was locked in a fixed position, the scale of  $C_3$  calibrated and the measurements made. When it was desired to use  $C_3'$  as the measuring condenser,  $C_3$  was locked and the small condenser scale was calibrated.

3.  $R_1$  is a non-inductive resistance made by filling a conical glass tube with "Manganin" solution (121 g. of mannitol plus 41 g. of boric acid). The resistance of this tube could be varied by varying the distance between the electrodes or by moving a plunger down into the ground glass conical part of the tube, thereby decreasing the cross section. The stem of the plunger fitted into a hard rubber cap which was threaded. The small thread on the screw of the cap made possible a very sharp setting of the resistance. This was extremely important when any great conductivity was possessed by the liquid being measured. In some cases it was found that turning the cap one or two mm., involving the very slight accompanying displacement of the plunger in the tube, entirely obscured the minimum. Previous workers have called attention to the importance of the resistance used to compensate the conductivity. It has been suggested that as the conductivity increased and the electrodes in the liquid resistance were moved closer together, a capacity was introduced in the resistance tube which involved an error in the capacity of the measuring condenser. That this is not the true explanation can easily be shown by a consideration of the voltage consumption in the measuring arm of the bridge. A simple calculation is sufficient to illustrate this point.

Consider the bridge, with capacities  $C_1$  and  $C_2$  balanced against capacities  $C_3$  and  $C_4$  the latter being shunted with resistances  $R_1$  and  $R_2$  respectively. Then  $Z_1/Z_2 = Z_3/Z_4$  where  $Z$  is the impedance; if  $C_1 = C_2$ , and both  $C_1$  and  $C_2$  are air condensers,  $Z_1 = Z_2$ , and therefore  $Z_3 = Z_4$ .

Let us suppose that  $C_4$  is composed of 2 concentric cylinders 0.2 cm. apart and having an electrode surface of 50 sq. cm. Furthermore, let the dielectric be alcohol having a dielectric constant of 25 and a specific conductivity of  $1 \times 10^{-7}$  mho.

The capacity of such a condenser is  $Ka/4\pi d$   $900,000 = 0.00055$  mf. The resistance of such a cell is therefore  $(50/0.2) \times 10^{-7} = 2.5 \times 10^{-5}$  mho  $= 0.4 \times 10^6$  ohm.

The impedance of the above capacity and resistance in parallel may be most easily calculated by obtaining the vectorial sum of the admittances due to capacity and resistance. The admittance due to capacity at a frequency of 1000 is  $2\pi \cdot 1000C = 2 \times 3.1416 \times 1000 \times 5 \times 10^{-10} = 3.1 \times 10^{-6}$ . Therefore the admittance of the combina-

tion is  $\sqrt{(2.5 \times 10^{-5})^2 + (3.1 \times 10^{-6})^2} = 2.52 \times 10^{-5}$ . The impedance is  $1/2.52 \times 10^{-5} = 0.396 \times 10^5$  ohm.

This calculation shows that the impedance of the whole bridge arm is largely determined by that of the resistance alone and that the quantity which we wish to measure, the capacity, only slightly affects the total impedance. In other words, an accurate measurement of capacity cannot be made at a frequency of 1000 cycles per second if the impedance due to resistance is less than that due to capacity. This is an important consideration for the determination of the limit of conductivity. It has been commonly overlooked in dielectric-constant measurements of conducting solutions.

4. In the fourth arm of the bridge was a condenser,  $C_4$ , shunted by a Mangani solution resistance. This condenser acted as a tare condenser and the resistance was used to balance the conductivity of the liquid when the dielectric cell condenser was placed on the  $C_3$  arm of the bridge in the differential method of measurement which was used. Our purpose in finally adopting the differential method was to eliminate any errors due to an unsymmetrical arrangement of the bridge such as different self-inductances of the wires, mutual capacities of the condensers, etc. Also by the differential method twice the ordinary displacement on the measuring scale is obtained for a given change in dielectric.

The dielectric cell was composed of two co-axial platinum cylinders, 2.2 cm.  $\times$  6.3 cm. and 1.9 cm.  $\times$  6.3 cm., respectively, which were set in the ground glass stopper of a glass cup. This cup was mounted on a hard rubber base. The platinum cylinders were firmly fastened at each end to prevent any possible displacement during a set of measurements. These cylinders as well as the cup were easily cleaned between measurements by washing several times with alcohol and ether and then drying in a stream of air. It was so arranged that the whole dielectric cell could be placed in a holder in a thermostat if at any time the accuracy of the work should demand close temperature control. The dielectric cell was arranged by means of a rocking commutator so that it could be placed in parallel first with  $C_4$  and a reading taken and then in parallel with  $C_3$  and the difference in reading taken. During the calibration of the scale and during any series of measurements,  $C_1$ ,  $C_2$ , and  $C_4$  were sealed,  $C_3$  being the only condenser whose capacity was changed.

The amplifier was a two-step type triode E to which a third step was added by means of an amplifying transformer and an electron tube, thus giving a 1000 fold amplification. The plates were charged at 40 volts from dry cells and the filaments were heated by a current of 0.7 ampere and 6 volts from lead storage cells. This amplifier was used in connection with a set of Baldwin wireless telephones. These telephones have non-adjustable mica diaphragms and were especially suited for wireless work for the reception of very weak signals. Their resistance was 2000 ohms. In any determination, the amplifier was adjusted by changing the temperature of the filaments to give the greatest sensitivity and then was not changed during an entire calibration and set of measurements. This was in keeping with the care always exercised during a set of readings to vary nothing but the liquid in the dielectric cell and the capacity of the measuring condenser. It was only by employing the greatest precaution along these lines that consistent and comparable results could be obtained. For instance, before the rocking commutator was used in the differential method of measurement, a wire was moved from  $C_4$  to  $C_3$  in order to change the dielectric cell from parallel with  $C_4$  to parallel with  $C_3$ . It was discovered that the movements of this fine short wire caused the shifting of the minimum many divisions on the recording scale. Again, before the final setting was made by the use of the vernier condenser lever operated at a distance from the bridge, it was found that effects produced by the operator's body either entirely obscured the minimum or shifted it a few hundred divisions.

The first set of measurements on the bridge was made for the purpose of determining the sensitivity of the apparatus. Before using the differential method it was found that we were able to get very sharp minima when the ratio of the condensers in the ratio arms was other than one to one. This made it possible to magnify the deflection of the dielectric cell on the measuring condenser. With benzene in  $C_4$ , the dielectric cell,  $C_3$  the measuring condenser gave in 4 experiments, 430, 430, 430, and 390; with ether it gave 840, 905, 1070, and 1205, respectively.

In the last measurement a change in dielectric of from 2.22 to 4.35 caused a change on the setting scale of the measuring condenser of 815 divisions, which means (setting to one division on the scale and one division is one millimeter) that one division on the scale is equivalent to a change in dielectric of 0.0026. These measurements could be made on  $C_3'$ . When made on  $C_3'$  which possessed a 5-fold sensitivity, one scale division was equivalent to a change in dielectric of 0.0005. No attempt was made to carry this study further as it was not desired to reach this sensitivity. For our measurements we needed a sensitivity which would keep the readings of a change in dielectric of from 2 to 26 on the scale.

A set of measurements was made by the differential method and the same satisfactory balancing of the bridge was obtained.

Investigation was next made of the effect of an added non-inductive resistance to an air condenser whose capacity was being measured by the differential method. This resistance was balanced out by a resistance in parallel to the condenser in the balancing arm.

	<i>a.</i>	<i>b.</i>	<i>a-b.</i>	<i>diff.</i>
Condenser alone .....	497	293	204	..
Condenser plus resistance in parallel .....	505	260	245	41

As the resistance decreased, the difference between the true capacity and the observed capacity increased. Next a 22,000-ohm resistance was shunted around the condenser whose capacity was being measured. As the capacity was increased, the amount that the minimum was shifted due to the shunted resistance decreased. It was also found that there was less shifting of the minimum due to the shunted resistance if the ratio condensers as 1:1. The reason for this can be seen from the following calculation.

If the impedance of the ratio arms is the same, *i. e.*, if  $C_1 = C_2$ , then  $C_3 = C_4$  in the presence of conductivity due to  $R$  only on condition that  $C_3$  is shunted with an equal resistance. On the other hand, if  $C_1$  does not equal  $C_2$ , the ratio of  $C_3$  to  $C_4$  will not equal the ratio of  $C_1$  to  $C_2$  even under the condition that  $R_3$  is equal to  $R_4$ . A single calculation is sufficient to bring out this point.

Let  $C/C_2 = a/b$ ; then  $Z_3/Z_4 = b/a$ ; or  $A_3/A_4 = a/b$  (1)  
 where  $Z$  is the impedance, and  $A$  is the admittance. Further let  $R_3 = R_4 = x$ .  $A$   
 = the vectorial sum of  $C_3 + (1/x)$ .

$$= \sqrt{C_3^2 + (1/x^2)}; \text{ and } A = \sqrt{C_4^2 + (1/x^2)}.$$

$$\text{From Eq. 1 } a \sqrt{C_4^2 + 1/x^2} = b \sqrt{C_3^2 + 1/x^2}.$$

$$\text{Squaring, } a^2 C_4^2 + \frac{a^2}{x^2} = b^2 C_3^2 + \frac{b^2}{x^2}$$

$$b^2 C_3^2 - \frac{a^2 - b^2}{x^2} = a^2 + C_4^2 \quad (2)$$

$$\frac{b^2 C_3^2}{a^2 C_4^2} = 1 + \frac{a^2 - b^2}{a^2 C_4^2 x^2}$$

$$\frac{C_3^2}{C_4^2} = \frac{a^2}{b^2} + \frac{a^2 (a^2 - b^2)}{b^2 a^2 C_4^2 x^2}$$

$$\frac{C_3}{C_4} = \frac{a}{b} + \sqrt{\frac{a^2 - b^2}{b^2}} - \frac{1}{C_4 x}. \quad (3)$$

From this general equation one can see that the ratio of  $C_3$  to  $C_4$  is equal to the ratio of  $C_1$  to  $C_2$  only when the product  $C_4 x$  is large. Inasmuch as  $C$  is the capacity of the condenser being measured we can increase the product only by working with dielectrics of small conductivities, that is of large values of  $x$ . In other words, it is possible to obtain a greater sensitivity by making the ratio of the ratio condensers greater than 1; however, this cannot be done for liquids having appreciable conductivity.

The effect of the introduction of the maximum conductivity of the Mangani resistance tubes shunted around an air condenser was studied. As shown by the following observation, no appreciable shifting of the minimum resulted.

	<i>a</i> .	<i>b</i> .	<i>a-b</i> .
Air condenser alone .....	1488	321	1167
Air condenser plus maximum conductivity of resistance tube .....	1498	330	1168

The same results were obtained when the dielectric cell was used.

Dielectric cell alone,

	<i>a</i> .	<i>b</i> .	<i>a-b</i> .
Empty .....	1636	1588	48
Filled with ether .....	1701	1523	178
Dielectric cell plus maximum conductivity of resistance tube,			
Empty .....	1633	1585	48
Filled with ether .....	1700	1522	178

In all measurements of dielectric constants only those liquids were measured whose conductivity could be balanced out with the tested Mangani solution resistances.

The condensers in the ratio arms were now set at 90, *i. e.*, at a ratio of 1:1, condensers  $C_1$ ,  $C_2$ , and  $C_4$  were sealed,  $C_3$  was locked into position and the scale on  $C_3$  was calibrated by filling the dielectric cell with the above liquids. The calibration curve is given on the chart with the curves for the dielectric measurements.



Liquid.	CALIBRATION DATA.			
	D. C.	a.	b.	a-b.
Carbon tetrachloride.....	2.25	1268	1160	108
Ether.....	4.35	1320	1115	205
$C_6H_6 + C_6H_5NO_2$ .....	15.9	1380	860	720
Alcohol.....	25.8	1795	640	1155

The following tables give the results of the dielectric measurements of the different mixtures with interpolation values from the curves. The points on the calibration curve were re-checked between measurements so as to assure no change in the values of the bridge. The liquids were not allowed to stand exposed to the air during a measurement, because in some cases the conductivity increase due to the absorption of water vapor from the air was such as to introduce an error in the observed value of the capacity of the dielectric cell. The conductivity of alcohol was observed to increase considerably upon exposure to the air for a few seconds. At the end of a half hour or less the conductivity had increased beyond that which could be balanced out with the maximum conductivity of the Manganin resistances.

#### DIELECTRIC CONSTANTS OF MIXTURES OF BENZENE IN ETHYL ALCOHOL

Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.
0	2.28	40	10.8	80	20.6
10	4.3	50	13.1	90	23.2
20	6.5	60	15.5	100	25.8
30	8.6	70	18.0		

#### DIELECTRIC CONSTANTS OF MIXTURES OF ETHER IN ALCOHOL.

Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.
0	4.35	40	10.9	80	20.6
10	5.7	50	13.1	90	23.2
20	7.2	60	15.5	100	25.8
30	8.9	70	18.0		

#### DIELECTRIC CONSTANTS OF MIXTURES OF CARBON TETRACHLORIDE IN ALCOHOL.

Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.
0	2.25	40	14.5	80	22.6
10	5.4	50	17.0	90	24.2
20	8.6	60	19.1	100	25.8
30	11.7	70	20.9		

### Summary.

1. A bridge method for the measurement of dielectric constants is described.

2. Preliminary measurements of the dielectric constants of mixtures of ethyl alcohol and benzene, ethyl alcohol and ether, and ethyl alcohol and carbon tetrachloride are given.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## ORGANOGEELS OF SILICIC ACID.

BY B. S. NEUHAUSEN AND W. A. PATRICK.

Received May 23, 1921.

As is well known Graham<sup>1</sup> was able to prepare silicic acid gels which contained large percentages of organic liquids, such as alcohol, ether, glycerine, and only very small amounts of water. Owing to the large percentage of organic liquids that were contained in the organogels, and from the ease with which he could replace one liquid by another by allowing the gel to soak in the liquid, *viz.*, transformation of an alcogel into an ether gel, Graham was led to some interesting conclusions: "The various organic liquids are capable of displacing the combined water of silicic acid hydrate, whether that hydrate is in the liquid or gelatinous condition, and give new products. The production of the compounds of silicic acid indicates the possession of a wider range of affinity by a colloid than could well be anticipated. Thus, of hydrated silicic acid the combined water leaves the acid to diffuse into the alcohol, and if the alcohol be repeatedly changed the *entire* water is thus removed, alcohol at the same time taking the place of the water in combination with the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Such changes illustrate the predominating influence of mass."

Because of Graham's experimental results and his conclusions which enjoy wide acceptance, the question arose whether we could prepare a hard gel composed of only silica and an organic liquid. This seemed very probable, since in the alcogel as prepared and analyzed by Graham there were 383 parts of alcohol to 1 part of water. It was thought that by heating the gel at a high temperature in a vacuum, an organic gel practically water-free could be obtained.

## Preparation of the Gels.

The hydrogel of silica was prepared in the usual way from water glass and hydrochloric acid. The gel was washed free from chlorides, squeezed to remove as much water as possible, and then placed in 95% alcohol. Another sample was put into C. P. acetone. After the gel had remained in the alcohol for 24 hours it was squeezed dry of liquid and transferred to a fresh sample of alcohol. This treatment was repeated four times. The gel was then placed in a sample of alcohol that had been refluxed over lime for several days, and allowed to stand for two days. This treatment with the anhydrous alcohol was repeated four times.

<sup>1</sup> Graham, *J. Chem. Soc.*, 17, 318 (1864); *Pogg. Ann.*, 123, 529 (1864).

A sample of the gel that had undergone the above treatment was heated in a vacuum of 5 mm. for 1 hour at 80°, 1 hour at 120°, and finally for 1 hour at 270°.

The acetone gel was put through a similar process. It was given four treatments of 24 hours' duration in c. p. acetone, and finally four treatments at 48-hour intervals in redistilled acetone (b. p. 56.5°).

A portion of the alcogel as it came from the last soaking in alcohol was transferred to redistilled benzene and allowed to remain in this liquid for 2 days. This treatment was repeated six times, when a sample failed to give the iodoform test for alcohol. This benzene gel was heated in a vacuum like the others.

### Analytical Results.

The three gels were analyzed by the regular combustion methods of organic chemistry. Towards the end of the combustion the boat containing the gel was heated to about 900° in order to drive all the water out of the gel. From the amounts of carbon dioxide and water formed, the percentages of alcohol, acetone, or benzene, as well as that of water in the gel were calculated. A typical analysis follows.

	I. G.	II. G.
Wt. of acetone gel .....	1.343	0.860
H <sub>2</sub> O produced by combustion .....	0.111	0.0712
CO <sub>2</sub> produced by combustion .....	0.115	0.0732
Calculated weight of acetone .....	0.0505	0.0322
Water from acetone .....	0.0470	0.0300
Excess water .....	0.0640	0.0412
% Acetone in gel .....	3.76	3.74
% Water in gel .....	4.76	4.78

The analytical results are tabulated below.

	% water.	%.
Alcogel	4.23	3.90 alcohol
Acetone gel	4.77	3.75 acetone
Benzene gel	4.31	3.82 benzene

### Discussion.

From the above results it is apparent that Graham was in error when he stated that it is possible to replace all the water from a silica hydrogel by other liquids. We have shown in this laboratory that silica gel may be heated to 300° in a vacuum produced by a Gaede pump for a period of 6 hours without reducing the water content below 4.8%. It is not surprising, therefore, that soaking in anhydrous alcohol as above described does not remove all the water. It is evident that the residual small percentage of water in silica gel is held with a force that exceeds that exhibited between the atoms of many stable compounds. Subsequent work in this laboratory has shown that this water can be removed at high

temperatures without affecting appreciably the structure of the gel as exhibited by its adsorption ability.

### Summary.

It is impossible to remove all the water from the hydrogel of silicic acid by repeated immersions in anhydrous alcohol, acetone, or benzene.

BALTIMORE, MARYLAND.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 370.]

## COMPOUND FORMATION AND CONDUCTIVITY IN SYSTEMS OF THE TYPES FORMIC ACID:METAL FORMATE AND SULFURIC ACID:METAL SULFATE.

BY JAMES KENDALL, HOWARD ADLER AND ARTHUR W. DAVIDSON.

Received June 6, 1921.

In a recent investigation<sup>1</sup> on systems of the types acid:ester, acid:ketone and acid:acid it has been shown that the specific conductivities of such binary mixtures increase regularly with increasing compound formation between the components. Strong support was thereby obtained for the validity of the hypothesis, formulated in earlier articles,<sup>2,3</sup> that ionization in solutions is primarily dependent upon the preliminary formation of unstable solvent-solute complexes. In subsequent communications<sup>4,5</sup> it has also been established that compound formation in systems of the general type  $HX:RX$  increases in extent with increasing diversity in the positions of the radicals H and R in the electrode potential series. The present work continues the study of systems of this type by examining how far the parallelism between compound formation and conductivity can be traced in them. As experimental material, the two series previously investigated with respect to compound formation (metal formates in formic acid and metal sulfates in sulfuric acid) have naturally been chosen.

Very accurate determinations upon the conductivities of the alkali and alkaline earth formates in anhydrous formic acid have been carried out by Schlesinger and his co-workers,<sup>6</sup> so that only a few additional data were required in this series. In the case of sulfuric acid:metal sulfate systems, the results of previous investigations proved to be much less dependable.

<sup>1</sup> Kendall and Gross, *THIS JOURNAL*, **43**, 1426 (1921).

<sup>2</sup> Kendall and Booge, *ibid.*, **39**, 2323 (1917).

<sup>3</sup> Kendall and Gross, *ibid.*, **43**, 1416 (1921).

<sup>4</sup> Kendall and Davidson, *ibid.*, **43**, 979 (1921).

<sup>5</sup> Kendall and Adler, *ibid.*, **43**, 1470 (1921).

<sup>6</sup> Schlesinger, *et. al.*, *ibid.*, **33**, 1924 (1911); **36**, 1589 (1914); **38**, 271 (1916); **41**, 72, 1921, 1934 (1919).

For correlation with these two series, we have also extensive data immediately available for a third series of precisely the same type—metal hydroxides in water. A sufficient variation in the acid radical X (from the strong acid  $\text{H}_2\text{SO}_4$ , through the intermediate acid  $\text{HCOOH}$ , to the very weak acid  $\text{HOH}$ ) is thus obtained to enable us to test the effect of changes in this radical upon the nature of the results, and to extend any generalizations deduced over the whole field  $\text{HX} : \text{RX}$ .

### Systems of the Type, Formic Acid : Metal Formate.

Schlesinger has demonstrated that the alkali formates are extensively dissociated in formic acid solution, and that very satisfactory ionization constants can be obtained for each salt through a wide range of concentrations without the application of any viscosity correction to the conductivity data. The alkali earth formates also<sup>6</sup> are highly ionized in anhydrous formic acid, and give good ionization constants throughout a somewhat more limited range if it is assumed that they behave, in moderately concentrated solutions, as uni-univalent electrolytes.<sup>7</sup> It is possible that the mutual cancellation of counterbalancing factors may account for this somewhat unexpected vindication of the Ostwald dilution law in both cases, but the ionization constants for the different salts as calculated by Schlesinger can certainly be safely utilized as indicative of the order of their strengths as bases<sup>8</sup> in formic acid solution, which is all that is needed for the purpose of the present investigation.

Conductivity determinations have here been carried out upon 3 salts not studied by Schlesinger, namely, barium, magnesium and lead formates. In order not to trench too deeply upon the field, no complete survey of the ionization equilibria of these salts in anhydrous formic acid has been undertaken. Only a limited concentration range has been examined in each case, and it has been assumed that within this range the three salts, like those investigated by Schlesinger, behave as uni-univalent electrolytes.

Measurements were made in a cell of the Freas type with platinized electrodes. A 3-meter Leeds and Northrup bridge was employed. Alternating current (1000 cycles per sec.) was obtained by means of a constant-speed high-frequency generator; the telephone used was tuned to the same frequency. The experiments were performed in a Freas thermostat at  $25 \pm 0.01^\circ$ . The formic acid used possessed a specific conductivity of  $7.3$  to  $7.5 \times 10^{-6}$  mhos, a value somewhat higher than that obtained by Schlesinger and Martin.<sup>9</sup> The preparation of anhydrous acid and pure salts was carried out as described in a previous article. While no exceptional degree of accuracy is claimed for the results given below, they are probably in error by less than 0.5%.

<sup>7</sup> As dibasic organic acids do, in water solution, until ionization is very extensive.

<sup>8</sup> Any salt  $\text{RX}$  in its own acid  $\text{HX}$  possesses the characteristics of a base (see Schlesinger and Calvert, *This Journal*, 33, 1933 (1911); Kendall, Davidson and Adler, *ibid.*, 43, 1481 (1921)).

<sup>9</sup> Schlesinger and Martin, *ibid.*, 36, 1590 (1914).

In the following table,  $c$  denotes the concentration of the solution in gram equivalents per liter,  $\chi$  is the specific conductivity in reciprocal ohms (the specific conductivity of the solvent being directly subtracted),<sup>10</sup>  $\lambda$  is the equivalent conductivity,  $\lambda_0$  the equivalent conductivity at infinite dilution (extrapolated according to the method employed by Schlesinger<sup>11</sup> and  $k$  the ionization constant of the salt at 25°. It will be evident, from the paucity of the data, that the values given in the last two columns are somewhat uncertain. They are to be regarded, indeed, only as indicative of the relative strengths of the three electrolytes examined.

TABLE I.  
CONDUCTIVITIES OF FORMATES IN FORMIC ACID AT 25°.

Salt.	$c$ .	$\chi$ .	$\lambda$ .	$\lambda_0$ .	$k$ .
(H.COO) <sub>2</sub> Ba	0.0474	0.002575	55.59	60.3	0.515
	0.0923	0.004827	52.26		
	0.2758	0.001185	42.96		
(H.COO) <sub>2</sub> Mg	0.0479	0.001683	35.14	40.6	0.266
	0.0919	0.002931	31.90		
	0.0477	0.001295	27.15		
(H.COO) <sub>2</sub> Pb				35.2	0.124
	0.1047	0.002387	22.80		

It will be seen that the ionization constant of the barium salt is about twice as large as that of the magnesium salt, and more than four times as large as that of the lead salt.

We may now proceed to examine how compound formation varies with ionization throughout the series. In Table II below the ionization constants for the various salts and the addition compounds actually isolated from each system are listed. The last column shows the depression of the freezing point of the acid in solutions containing 5 mol % of dissolved salt.

IONIZATION AND COMPOUND FORMATION.		FORMATES IN FORMIC ACID SOLUTION.	
Salt.	Ionization constant, 25°.	Compounds isolated (A = salt; B = acid).	$\Delta T$ (5 mol % salt).°
H.COO.NH <sub>4</sub>	1.230	AB <sub>3</sub> ; AB	5.9
H.COOK	1.090	AB <sub>3</sub> ; AB <sub>2</sub> ; AB	6.6
H.COONa	0.810	AB <sub>2</sub> ; AB	5.9
H.COOLi	0.557	....	4.9
(H.COO) <sub>2</sub> Ba	0.515	AB	8.5
(H.COO) <sub>2</sub> Ca	0.422	....	insoluble
(H.COO) <sub>2</sub> Mg	0.266	....	insoluble
(H.COO) <sub>2</sub> Pb	0.124	....	insoluble

<sup>a</sup> The ideal freezing-point depression for formic acid containing 5 mol % solute is 3.3°.

<sup>10</sup> Following Schlesinger's procedure. The accuracy of this method is open to serious question (as discussed in the text later), but in any case the effect is here extremely small.

<sup>11</sup> Schlesinger and Mullinix, THIS JOURNAL, 41, 74 (1919).

The rule that ionization parallels compound formation in extent is evidently generally applicable throughout the series. The strongest bases each give several compounds, the weakest bases do not show a single sample of an isolable acid salt. Two minor discrepancies in the order of compound formation (potassium giving 3 compounds to 2 of ammonium, barium one to none of lithium) may plausibly be referred to changes in the order of basic strengths with temperature. The ionization constants tabulated refer to 25° while the compounds are isolated at much lower temperatures, and Schlesinger and Coleman<sup>12</sup> have found that the temperature coefficient of the ionization constant in certain cases is very large.

As has been pointed out previously,<sup>13</sup> however, compounds may be existent in a solution without making their appearance on the freezing-point diagram as stable solid phases. A more trustworthy method of establishing the relative extent of compound formation for the different formates in formic acid solution is fortunately available in the comparison of the depressions which they induce in the freezing point of the acid itself.<sup>14</sup> The ideal freezing-point depression curve for formic acid<sup>15</sup> and

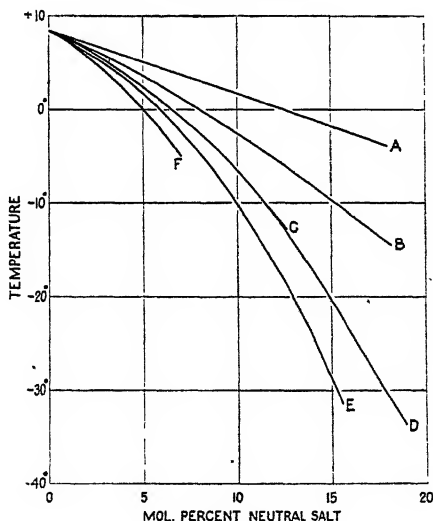


Fig. 1.—Freezing-point depression curves. Formic acid as solvent. A=ideal curve; B=lithium formate; C=sodium formate; D=ammonium formate; E=potassium formate; F=barium formate.

<sup>12</sup> Schlesinger and Coleman, *THIS JOURNAL*, 38, 278 (1916).

<sup>13</sup> Kendall, Booge and Andrews, *ibid.*, 39, 2308 (1917).

<sup>14</sup> Compare Kendall and Booge, *ibid.*, 38, 1730 (1916).

<sup>15</sup>  $Q$  (the molar heat of fusion) is taken as 2420 cal. (Berthelot, *Compt. rend.*, 78, 716 (1874)).

the experimental curves obtained on addition of the various salts are shown in the accompanying diagram. The depressions for a single fixed concentration of salt (5 mol %) are also compared in Table II (p. 1848).

For the uni-univalent salts, the deviations from the ideal curve fall in the order  $K > (NH_4 \text{ or } Na) > Li$ , corresponding with the order of stability and complexity in compound formation. The extensive ionization of the salts in formic acid solution, of course, accounts for a great part of the abnormally large depressions obtained, but the data at the higher concentrations show clearly the additional effect of actual removal of solvent by compound formation. Thus the potassium salt gives twice the normal depression at 5 mol % concentration, while at 15 mol % the depression is nearly 4 times that calculated from the ideal curve. Compound formation in this case must be very extensive, as is evidenced not only by the compounds definitely isolated but by the transference-number data of Schlesinger and Bunting.<sup>16</sup> With the other uni-univalent salts the effect is appreciably smaller, particularly in the case of lithium. In view of the position of this metal at the head of the electrode potential series, indeed, the comparative weakness of its formate as a base and its corresponding inability to form isolable acid salts cannot be allowed to pass without comment, although no adequate explanation can be adduced at present.<sup>17</sup>

Of the 4 remaining salts of the type  $(H.COO)_2Me''$ , only those of barium and calcium are sufficiently soluble to give reliable comparable data. The freezing-point depression curve for the barium salt (see Curve F on the diagram; the calcium salt practically duplicates this curve up to 1.5 mol %) is more abnormal even than that for the potassium salt. Thus the observed depression for a solution of 5 mol % concentration is  $8.5^\circ$ , compared with a calculated value of  $3.3^\circ$ . In view of this, it appears very improbable that Schlesinger's assumption that the alkaline earth formates behave, in moderately concentrated solutions, as uni-univalent electrolytes can be valid, since only by assuming a compound of truly enormous complexity could the position of the barium curve be accounted for on this basis. If we admit that the salt can give 3 ions by dissociation, however, the observed depressions are just about what might be expected.

#### Systems of the Type Sulfuric Acid : Metal Sulfate.

The same experimental procedure was employed as in the case of formic acid systems, except that sulfuric acid of minimum conductivity was made up directly in the cell (by gradual addition of acid slightly under 100%

<sup>16</sup> Schlesinger and Bunting, *THIS JOURNAL*, 41, 1934 (1919).

<sup>17</sup> The question will be taken up in a later article, in connection with the atomic volume factor.



to acid slightly over 100%) in order to avoid contamination with atmospheric moisture during transfer. The specific conductivity of the acid so prepared varied from 0.01035 to 0.01050 reciprocal ohm at 25°. Lichty<sup>18</sup> in a very careful investigation, obtained the value 0.01041; according to his conductivity-composition data, the acid here used contained less than 0.005 % of water.

The conductivity results for a series of sulfates at a single fixed concentration (0.04 gram equivalents per liter) in the 100% acid are presented in Table III below. In the preparation of this table, the method adopted by previous investigators for the evaluation of the specific conductivity of the salt has been followed, the specific conductivity of the pure solvent being subtracted directly from that of the solution.

TABLE III.  
CONDUCTIVITIES OF SULFATES IN SULFURIC ACID AT 25°.

Salt.	Solution.	Specific conductivity		Equiv. cond. of salt.
		Solvent.	Due to salt.	
Na <sub>2</sub> SO <sub>4</sub>	0.01206	0.01044	0.00162	40.5
BaSO <sub>4</sub>	0.01149	0.01038	0.00111	27.8
CaSO <sub>4</sub>	0.01210	0.01043	0.00167	41.8
MgSO <sub>4</sub>	0.01130	0.01043	0.00087	21.8
ZnSO <sub>4</sub>	0.01207	0.01039	0.00168	42.0
PbSO <sub>4</sub>	0.01237	0.01050	0.00187	46.8
Ag <sub>2</sub> SO <sub>4</sub>	0.01208	0.01035	0.00173	43.3

Previous measurements upon the conductivities of neutral sulfates in 100% sulfuric acid have been carried out by Walden,<sup>19</sup> Hantzsch,<sup>20</sup> Bergius<sup>21</sup> and Poma.<sup>22</sup> The results obtained are extremely discordant; thus for sodium sulfate at the concentration examined above the interpolated equivalent conductivity values of these 4 observers are 97, 31, 46 and 14, respectively. From results of this order of accuracy, it is obviously futile to attempt to draw any conclusions.

The main source of error is undoubtedly due to the solvent correction, which varies from 80 to 90% of the total conductivity. A small error in this correction will introduce a very significant error in the equivalent conductivity of the salt, and the tacit assumption that the specific conductivity of the pure solvent is unchanged on addition of neutral salt is quite as unjustified as would be the corresponding assumption that the ionization equilibrium of water is unaffected by addition of a base. If we knew the mobilities of the various ions existent in any given solution, it might be possible for us to apply more dependable solvent corrections,<sup>23</sup>

<sup>18</sup> Lichty, *THIS JOURNAL*, 30, 1841 (1908).

<sup>19</sup> Walden, *Z. anorg. Chem.*, 29, 383 (1902).

<sup>20</sup> Hantzsch, *Z. physik. Chem.*, 61, 293 (1908).

<sup>21</sup> Bergius, *ibid.*, 72, 338 (1910).

<sup>22</sup> Poma, *J. chim. phys.*, 10, 187 (1912).

<sup>23</sup> Compare Kendall, *THIS JOURNAL*, 39, 7 (1917).

but at the present time we cannot do more than concede that all of the salts investigated give conductivity values indicating approximately the same degree of ionization at the concentration here studied. To deduce differences in the basic ionization constants of sulfates in sulfuric acid from the different equivalent conductivities given in the last column of Table III above would obviously be quite unwarranted. It may be noted here that differences in the extent of acid salt formation are also less pronounced in the sulfuric acid than in the formic acid series.<sup>5</sup>

In the third series for which data are available, however, (namely systems of the type water:metal hydroxide) differences in basic ionization constants and in the stability and complexity of hydrates are exceedingly great. At the head of the electrode potential series we have the strongest bases, the alkali hydroxides, each of which gives several stable hydrates. The hydroxides of all metals in the neighborhood of hydrogen are scarcely ionized at all in aqueous solution. At the foot of the series we find an increase in basic strength again becoming apparent, silver hydroxide being a moderately strong base. Solubility variations are similarly much more marked among the hydroxides than in either the formate or the sulfate series.<sup>24</sup>

From the results of this and previous articles it may be concluded, therefore, that systems of the general type  $HX : RX$  supply strong support for the fundamental relationships suggested between diversity of chemical character (*i. e.*, electrode potential difference between R and H), compound formation, solubility and ionization. Variations in all of these properties, however, and particularly variations in ionization, can be much more clearly traced when X is a weakly acidic radical. With hydroxides enormous differences are evident, with formates the gradations are much less steep (for example, the ionization constant of the potassium salt is only 9 times that of the lead salt), with sulfates the solvent correction error is sufficient to mask any differences in ionization entirely. The examination of intermediate series (such as cyanides, acetates or fluorides) would undoubtedly add results of great interest in this connection, but must be deferred for the present in favor of work on systems of other types.

### Summary.

Conductivity measurements have been carried out for neutral formates in formic acid solution and for neutral sulfates in sulfuric acid solution. In the case of the formates, it has been possible to obtain direct confirmation for the parallelism between the extent of compound formation and ionization. For the sulfates, however, the uncertainty of the solvent correction is so great as to obscure the results.

<sup>24</sup> Compare Kendall, Davidson and Adler, *THIS JOURNAL*, 43, 1490 (1921).

Variations in compound formation, solubility and ionization in systems of the general type  $HX : RX$  are all, indeed, more extreme the weaker the acidic radical  $X$ . Hydroxides in water differ more widely than formates in formic acid, these again are more diverse than sulfates in sulfuric acid.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 371.]

## COMPOUND FORMATION IN PHENOL : CRESOL MIXTURES.

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Received June 6, 1921.

It has been shown in previous articles<sup>1</sup> that the extent of addition compound formation in binary liquid mixtures is controlled primarily by "chemical contrast," the stability of complexes increasing uniformly with the differences in character (*i. e.*, in the positive or negative nature of the constituent groups) of the two components. A great number of systems of very diverse types have been carefully examined, and incidentally no fewer than 101 new compounds have been discovered. To all of these systems the simple generalization given above is directly applicable, except to systems containing phenols.

Several times in the course of the work<sup>2</sup> abnormal results with phenols have been noted and tentative explanations, such as the existence of phenol in two tautomeric forms of widely different acidic strengths, proposed. Recently, Dawson and Mountford<sup>3</sup> have made a thorough investigation of compound formation in systems of the type phenol: cresol by the freezing-point method, obtaining definite compounds in 5 out of 6 cases. This they considered as rather remarkable in view of the close chemical similarity of the components, and concluded that "the relations disclosed by the freezing-point diagrams are consequently not in accord with what should have been anticipated on the basis of the views advocated by Kendall." The fact that the uniform abnormality of the phenols had already been emphasized was apparently overlooked.

A similar study of phenol: cresol systems by Fox and Barker<sup>4</sup> leads to quite contradictory results, a stable compound being isolated in only one of the six mixtures examined. This discrepancy is in all probability due to inadequate purification of the materials employed by Fox and Barker, and to the general inferiority of their method. In view of the extreme care exercised by Dawson and Mountford in all details, there is no reason

<sup>1</sup> For a summary of results and conclusions, see Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2304 (1917).

<sup>2</sup> Kendall, *ibid.*, 36, 1241 (1914); 38, 1317 (1916); Kendall, Booge and Andrews, *loc. cit.*, p. 2306.

<sup>3</sup> Dawson and Mountford, *J. Chem. Soc.*, 113, 923 (1918).

<sup>4</sup> Fox and Barker, *J. Chem. Ind.*, 37, 268 (1918).

to doubt the accuracy of their freezing-point data. The fact established by Fox and Barker, however, that the boiling-point curves of phenol-cresol mixtures show very little departure from the linear, is not what would be expected from systems in which addition compounds are present in appreciable quantity.

The present paper gives the results of further investigations on the physico-chemical properties of phenol-cresol mixtures, undertaken in the hope either of bringing these systems into line with the rest, or of obtaining some clue to the source of the abnormalities which they exhibit.

### Conductivity Measurements.

Kendall and Gross have demonstrated, in a recent article,<sup>5</sup> the validity of the general rule that compound formation and ionization in solutions proceed in parallel. For several series of binary organic mixtures it has been established experimentally that an increase in compound formation is regularly accompanied by a similar increase in specific conductivity. Where the extent of compound formation was known to be minute, the conductivity was almost immeasurable; as compound formation increased in amount, the conductivity became appreciable; where combination was extensive, the conductivity was very markedly increased.

As the first line of attack in the present work, it was consequently decided to determine the specific conductivity-composition curves of phenol-cresol mixtures. The essential principles of the experimental method employed have already been described by Kendall and Gross. The specific conductivities of the pure substances and solutions here under examination proved to be so extremely small, however, that some additional refinements in technique were necessary in order to obtain the required degree of accuracy in the experimental results.

**Conductivity Apparatus.**—The cell finally adopted was a 6-cylinder cell of the Beans and Eastlack type,<sup>6</sup> with a constant of 0.001426. The electrodes consisted of concentric platinum cylinders, 1 mm. apart, sand-blasted and connected alternately. With this cell it was possible to obtain very satisfactory sound minima with solutions of conductivity  $1.0 \times 10^{-9}$  mhos. Platinized electrodes could not be used, since in the presence of platinum black phenol-cresol solutions rapidly turn yellow, with a measurable increase in conductivity.

The bridge employed was a 4.70-meter circular slide-wire instrument, well-grounded and carefully calibrated. The resistance coils, up to 1000 ohms, were bifilar wound; those over 1000 ohms were of the Curtis type. A Vreeland oscillator gave a pure sine-wave alternating current of 1000 cycles per second. A high-resistance telephone receiver was used. The capacity of the cell was balanced out by means of a rotary air condenser connected in parallel with the resistance coils.

Most of the measurements were carried out in a large Freas thermostat, regulated to  $25^{\circ} \pm 0.005^{\circ}$ . Many of the solutions which normally

<sup>5</sup> Kendall and Gross, *THIS JOURNAL*, 43, 1426 (1921).

<sup>6</sup> Beans and Eastlack, *ibid.*, 37, 2674 (1915).

freeze at a higher temperature could be supercooled sufficiently to enable direct determinations at  $25^{\circ}$  to be made. With pure phenol and mixtures very rich in phenol, however, solidification could not be prevented in the presence of the sand-blasted electrodes, although viscosity measurements at  $25^{\circ}$  were later successfully accomplished. To complete the specific conductivity curves for phenol-cresol mixtures at  $25^{\circ}$  it was therefore necessary to perform experiments for these concentrations at higher temperatures and extrapolate the results.<sup>7</sup> For this purpose 2 smaller thermostats, regulated to  $40^{\circ} \pm 0.05^{\circ}$  and  $50^{\circ} \pm 0.10^{\circ}$ , respectively, were fitted up. Linear extrapolation was assumed to be valid over the small temperature range involved.<sup>8</sup> While this assumption is probably not strictly accurate, the values so obtained exhibit very good agreement with the direct measurements at  $25^{\circ}$ , as may be seen by referring to Fig. 1. In this diagram, the extrapolated sections of the various curves are indicated by broken lines.

Mixtures were made up by direct weighing, with the use of a Lunge pipet. The compositions as given in the tables below are accurate to within  $\pm 0.05\%$ . The specific conductivity data themselves possess a *relative* accuracy of the order of  $0.1\%$ , but owing to the impossibility of compensating exactly for inductance and capacity effects under the conditions of experiment, no claim is made for so high a degree of accuracy in their *absolute* values.

**Purification of Materials.**—As in the work of Kendall and Gross, it was found that the presence of impurities in quantities insufficient to exert any appreciable influence upon the freezing point or boiling point frequently involved a very considerable change in specific conductivity. A constant specific conductivity was therefore made the final criterion of purity.

In the case of each substance used, the purest material obtainable was repeatedly fractionated from special stills of Pyrex glass.<sup>9</sup> A middle fraction of constant freezing point usually gave a product of constant specific conductivity after 3 to 6 additional fractionations. In view of the hygroscopic nature of the materials under study and of the marked influence exerted by traces of water upon their specific conductivities, the last fractionations and conductivity determinations were restricted entirely to cold, dry days. The sensitivity of the materials towards moisture undoubtedly constitutes the chief source of error in the whole of the experimental work, and all possible precautions were taken to minimize its effect upon the results.

<sup>7</sup> Compare Kendall and Gross, *THIS JOURNAL*, 43, 1428 (1921).

<sup>8</sup> Compare Kendall and Brakeley, *ibid.*, 43, 1830 (1921).

<sup>9</sup> It was found that addition of a small quantity of anhydrous powdered sodium carbonate was very beneficial in accelerating the elimination of impurities.

**The System Phenol: *o*-Cresol.**—A c. p. sample of phenol, after about 20 fractional distillations, gave a final product of specific conductivity  $11.98 \times 10^{-8}$  at  $40^\circ$  and  $14.07 \times 10^{-8}$  at  $50^\circ$ . The only previously recorded value is that of Riesenfeld,<sup>10</sup>  $43 \times 10^{-8}$  at  $43^\circ$ . The freezing point obtained with our material was  $39.70^\circ \pm 0.02^\circ$ , identical with that found by Morgan and Egloff<sup>11</sup> for a specially prepared and purified sample. Several investigators have reported considerably higher values for unpurified specimens of phenol,<sup>12</sup> which would appear to indicate that commercial phenol is apt to contain an impurity which raises its fusion point. The original material here employed, indeed, gave a freezing point higher than that of the final product.

Pure *o*-cresol was obtained from a c. p. product by similar continued fractionation, the final material possessing a specific conductivity of  $0.127 \times 10^{-8}$  at  $25^\circ$  and a freezing point of  $30.60^\circ \pm 0.02^\circ$ . No previous measurements of the conductivity have been made; for the freezing point the most reliable recorded value<sup>3</sup> is  $30.45^\circ$ .

The conductivity results for the various mixtures examined at  $25^\circ$  are presented in Table I. The compositions of the solutions are expressed in molecular percentages throughout. The viscosity data which are appended will be discussed later.

TABLE I.

PHENOL: <i>o</i> -CRESOL.					
Mol. % phenol.	Spec. cond. $\times 10^8$ .	Viscosity.	Mol. % phenol.	Spec. cond. $\times 10^8$ .	Viscosity.
0.0	0.127	0.07608	69.27	2.583	0.08645
13.43	0.375	0.07835	75.79	3.321	0.08731
19.73	0.415	0.07930	80.03	4.196	0.08757
30.00	0.612	0.08099	87.30	5.422	0.08825
38.81	0.693	0.08235	90.10	6.183	0.08851
49.10	0.885	0.08404	100.00	8.84	0.08945
62.83	1.686	0.08565			

**The System Phenol: *m*-Cresol.**—Pure *m*-cresol was prepared by repeated fractionation from a standard c. p. sample. The specific conductivity of the final product was  $1.397 \times 10^{-8}$  at  $25^\circ$ ; its freezing point was  $11.10^\circ \pm 0.02^\circ$ . The highest value for the freezing point previously reported<sup>13</sup> is  $10.9$ ; no conductivity measurements are available for comparison.

<sup>10</sup> Riesenfeld, *Z. physik. Chem.*, **41**, 346 (1902).

<sup>11</sup> Morgan and Egloff, *THIS JOURNAL*, **38**, 844 (1916).

<sup>12</sup>  $42.4^\circ$  was found for a Kahlbaum sample (Kendall and Carpenter, *ibid.*, **36**, 2498 (1914)).

<sup>13</sup> Kendall, *THIS JOURNAL*, **38**, 1315 (1916). Dawson and Mountford employed a product with f. p.  $10.0^\circ$ ; Fox and Barker used material with a very much lower freezing point, presumably containing about 15% *p*-cresol (see Dawson and Mountford, *Ref. 3*, p. 924).

TABLE II.

PHENOL: *m*-CRESOL.

Mol. % phenol.	Spec. cond. $\times 10^8$ .	Viscosity.	Mol. % phenol.	Spec. cond. $\times 10^8$ .	Viscosity.
0.0	1.397	0.1342	63.52	4.197	0.09961
12.59	1.592	0.1250	73.25	5.094	0.09698
24.49	1.887	0.1169	81.90	5.923	0.09398
31.37	2.175	0.1131	89.21	6.810	0.09206
38.48	2.587	0.1095	93.01	7.431	0.09105
45.02	2.988	0.1070	100.00	8.84	0.08945
51.74	3.379	0.1040			

**The System Phenol: *p*-Cresol.**—The preparation of pure *p*-cresol from several standard c. p. samples was unsuccessfully attempted, the elimination of traces of *m*-cresol (which possesses almost exactly the same boiling point)<sup>14</sup> not being possible. Finally a satisfactory product was obtained by diazotizing pure *p*-toluidine<sup>15</sup> (f. p., 43.0°), distilling with steam, extracting the distillate with ether, and drying and fractionating the extract as described above. The specific conductivity of the final material was  $1.378 \times 10^{-8}$  at 25°; it gave a freezing point of  $34.55 \pm 0.02^\circ$ . Practically the same freezing-point value was obtained in previous researches of this series;<sup>13,12</sup> Dawson and Mountford, in their work, used a sample with f. p. 34.15°. No previous determinations of specific conductivity are recorded in the literature.

*p*-Cresol was found to be much more sensitive to light than its homologs, even a carefully purified specimen turning yellow in the course of a day if kept exposed. The data here presented were obtained with the use of freshly prepared material throughout.

TABLE III.

PHENOL: *p*-CRESOL.

Mol. % phenol.	Spec. cond. $\times 10^8$ .	Viscosity.	Mol. % phenol.	Spec. cond. $\times 10^8$ .	Viscosity.
0.0	1.378	0.1474	63.85	4.972	0.1042
15.98	2.210	0.1327	75.87	5.863	0.09835
31.91	3.012	0.1218	87.83	7.151	0.09463
38.51	3.423	0.1175	100.00	8.84	0.08945
52.18	4.201	0.1099			

**Systems containing Two Cresols.**—In Tables IV to VI (p. 1858), the conductivity and viscosity results for binary cresol mixtures are given.

<sup>14</sup> The b. p. (under 760 mm. pressure) of *m*-cresol is 202.1°, of *p*-cresol, 202.5°. In the cases of phenol and *p*-cresol, the differences in b. p. are sufficient to permit of systematic fractionation (see Dawson and Mountford, *J. Chem. Soc.*, 113, 937 (1918)).

<sup>15</sup> The reaction was carried out in 6 molar HCl solution by slow addition of the theoretical amount of sodium nitrite, the temperature being maintained below 10° and rapid admixture being ensured by vigorous stirring. When the reaction was complete the temperature was very gradually raised to 40° and the solution allowed to stand overnight before distilling with steam.

TABLE IV.

*o*-CRESOL: *m*-CRESOL.

Mol. % <i>o</i> -cresol.	Spec. cond. $\times 10^8$ .	Viscosity.
0.0	1.397	0.1342
15.37	1.134	0.1216
30.61	0.977	0.1109
35.36	0.874	0.1075
39.54	0.767	0.1050
50.60	0.633	0.09939
63.71	0.362	0.09208
76.08	0.184	0.08582
88.03	0.178	0.08086
100.00	0.127	0.07608

TABLE V.

*o*-CRESOL: *p*-CRESOL.

Mol. % <i>o</i> -cresol.	Spec. cond. $\times 10^8$ .	Viscosity.
0.0	1.378	0.1474
15.47	0.726	0.1327
29.99	0.601	0.1200
35.25	0.553	0.1163
42.33	0.507	0.1103
52.56	0.410	0.1030
63.04	0.344	0.09612
75.73	0.190	0.08854
87.50	0.188	0.08209
100.00	0.127	0.07608

TABLE VI.

*m*-CRESOL: *p*-CRESOL.

Mol. % <i>m</i> -cresol.	Specific cond. $\times 10^8$ .	Viscosity.	Mol. % <i>m</i> -cresol.	Specific cond. $\times 10^8$ .	Viscosity.
0.0	1.378	0.1474	62.38	1.551	0.1373
13.88	1.495	0.1450	67.83	1.512	0.1369
24.61	1.603	0.1432	70.71	1.449	0.1361
30.03	1.628	0.1425	73.73	1.442	0.1360
45.20	1.560	0.1400	82.67	1.378	0.1352
48.23	1.567	0.1393	91.35	1.384	0.1346
55.21	1.583	0.1385	100.00	1.397	0.1342

The specific conductivity results given in the above tables are represented graphically in Fig. 1. Curves I to III show the data for mixtures of phenol with the cresols, Curves IV to VI the data for binary cresol mixtures.

It will be immediately evident, from inspection of this diagram, that the specific conductivities of all of the solutions examined are very little

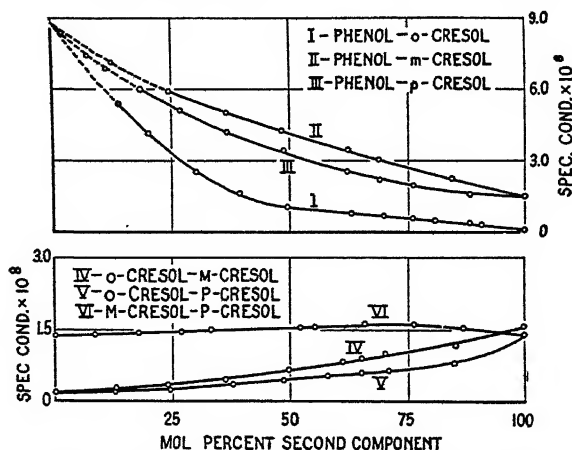


Fig. 1.—Specific conductivity-composition curves.



different from those of the pure components.<sup>16</sup> This type of curve, according to the predictions of Kendall and Gross,<sup>17</sup> is characteristic of all mixtures in which the two components are essentially similar in character. In such mixtures little or no increase in molecular complexity through compound formation is to be expected. Hence the observed conductivity of any solution should not differ significantly (if the parallelism between molecular complexity and ionization is accepted) from that obtained by linear extrapolation from the specific conductivities of its components.

The conductivity results here obtained are therefore in apparent contradiction with the freezing-point results of Dawson and Mountford, and in agreement with the generalizations formulated in previous papers of this series. This discrepancy will be discussed more fully below, after the work on some other physical properties of phenol-cresol mixtures has been described. The investigation of the viscosity-composition curves of these systems was chosen as the second line of attack in the present work, in view of the marked effect of changes in molecular complexity upon the viscosity.

### Viscosity Measurements.

Viscosity curves for binary liquid mixtures fall, in general, into three distinct types.<sup>18</sup> The ideal curve, given by solutions in which no interactions at all take place on mixtures of the components, is not linear but appreciably sagged. Where compound formation occurs on admixture, the viscosity (owing to the production of more viscous complexes) is abnormally high; if compound formation is extensive the curve may even exhibit a *maximum*. Where disassociation of an associated component takes place on admixture, the viscosity (owing to the production of less viscous molecules) is abnormally low; if disassociation is extensive the curve may even exhibit a *minimum*. In certain cases both compound formation and disassociation effects may be existent, producing a curve of a "pseudo-ideal" type.<sup>19</sup> A brief consideration of the chemical character of the components will suffice, however, to enable us to distinguish such a system from one which is truly ideal. Usually, also, one effect will predominate sufficiently to give a curve quite distinct from the normal type.

It was hoped, therefore, that a study of the viscosity curves of phenol:cresol systems would either make possible a decision between the apparently conflicting conclusions drawn from freezing-point and conductivity measurements, or indicate a means of reconciliation.

<sup>16</sup> The curve for the system *m*-cresol : *p*-cresol differs slightly from the 5 others, exhibiting an exceedingly small flat maximum, but in view of the extremely small conductivities given by this system throughout, no special significance is attached to this fact.

<sup>17</sup> Kendall and Gross, *THIS JOURNAL*, **43**, 1420 (1921).

<sup>18</sup> See Kendall and Monroe, *ibid.*, **43**, 115 (1921).

<sup>19</sup> Compare Kendall and Brakeley, *ibid.*, **43**, 1831 (1921).

The apparatus used for the determination of viscosities was of the Bingham type,<sup>20</sup> the experimental procedure being essentially as described in previous work.<sup>21</sup>

Very extensive investigations have recently been carried out by Bramley<sup>22</sup> on the viscosity of systems of the general type phenol : aniline. The viscosities and densities obtained by us for phenol and the cresols may be compared with the results of Bramley by reference to the following table. Density data by Dawson and Mountford are also included.

	Phenol.	o-Cresol.	m-Cresol.	p-Cresol.
$\eta_{25^\circ}$ (Bramley).....	0.0883	0.07620	0.1240	0.1413
(Kendall and Beaver).....	0.08945	0.07608	0.1342	0.1474
$d_4^{25}$ (Bramley) .....	1.0710	1.0440	1.0293	1.029
(D. and M.) .....	1.0710	1.0415	1.0295	1.0295
(K. and B.) .....	1.0708	1.0414	1.0298	1.0295

It will be seen that the agreement is not all that could be expected in every case. In view, however, of the extremely careful methods of purification employed in the present work, we believe our values to be more reliable.

The relative accuracy of the viscosity data presented in Tables I to VI above is  $\pm 0.2\%$ . With the apparatus employed, a somewhat higher degree of precision is attainable for most substances, but the temperature coefficient of viscosity of the liquids here examined is extremely high, approximately 10% per degree.<sup>22</sup> Very accurate density determinations are not necessary for the evaluation of viscosities with the Bingham type of instrument.<sup>23</sup> Consequently, after it had been found for each system that the density of an approximately equimolecular mixture was, within error limits, identical with that calculated from the densities of its components, it was assumed that no appreciable contraction occurred on admixture in any case,<sup>24</sup> and the densities for the remaining solutions were obtained by linear interpolation from the specific volume-weight composition curves.

The viscosity results for the 6 systems are reproduced in graphic form in the accompanying diagram Fig. 2. From inspection of the curves, it is again immediately evident that no appreciable change in average molecular complexity occurs on admixture in any system. The curves are apparently very near to the ideal type.

<sup>20</sup> Bingham, *J. Ind. Eng. Chem.*, 6, 233 (1914); Bingham, Schlesinger and Coleman, *THIS JOURNAL*, 38, 27 (1916).

<sup>21</sup> Kendall and Monroe, *ibid.*, 39, 1787 (1917).

<sup>22</sup> Bramley, *J. Chem. Soc.*, 109, 434 (1916).

<sup>23</sup> The density enters into the working formula only in a correction factor (approximately 1% of the total).

<sup>24</sup> This assumption is in agreement with the actual density determinations carried out by Fox and Barker (*J. Soc. Chem. Ind.*, 36, 845 (1917)) with less pure materials.

When it is remembered, however, that we have independent evidence from other physical properties<sup>25</sup> that phenol and the cresols are highly

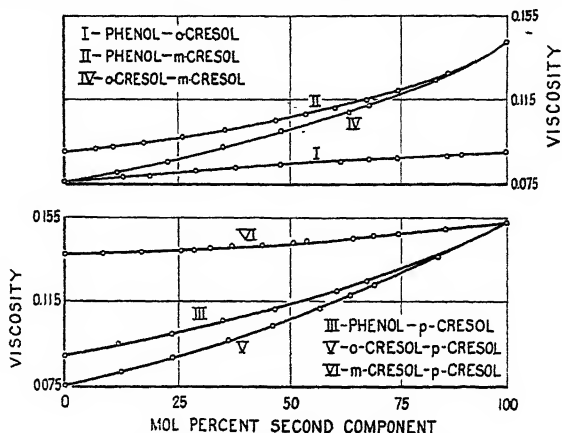


Fig. 2.—Viscosity-composition curves.

associated liquids in the pure state, it follows that this approximation to the normal type of curve must be due to the mutual compensation of the two opposing effects discussed above—compound formation and disassociation. Neither effect is here predominant; combination between the compounds appears to be practically counterbalanced by mutual depolymerization, leaving the average molecular complexity substantially unchanged.

To obtain confirmation of this point of view, a third line of attack was formulated, namely, the determination of the molecular weights of the pure substances, and the average molecular weights of certain of their binary mixtures, in an inert solvent.

### Molecular Weight Determinations.

The freezing point of a pure liquid, on addition of an ideal solute, will be depressed according to the equation<sup>26</sup>  $\ln x = (-Q/RT_o) \cdot (\Delta T/T)$  (where  $x$  is the mol fraction of solvent in the solution,  $Q$  the mol heat of fusion of the solvent,  $T_o$  and  $T$  the absolute freezing points of the pure solvent and the solution respectively,  $\Delta T$  the freezing-point depression, and  $R$ , 1.9852). If the solute is not ideal but associated, its average molecular weight in any solution of known composition can be calculated from the above equation<sup>27</sup> by substituting the experimentally determined value for  $\Delta T$  and solving for  $x$ .

<sup>25</sup> See Turner, "Molecular Association," 1915; also references in text later.

<sup>26</sup> Roozeboom, "Heterogene Gleichgewichte," 2, 273 (1904).

<sup>27</sup> Compare Washburn and Read, *THIS JOURNAL*, 41, 729 (1919). The error involved in the application of the simpler Raoult equation to the determination of molecular weights at high concentrations of solute is quite considerable.

As a suitable solvent, benzene was selected. The ideal freezing-point depression curve for this liquid has already been indicated in a previous article.<sup>21</sup> The benzene employed in the present work was very carefully prepared by repeated fractionation of a thiophene-free sample, dried over sodium. It possessed, within error limits, the same physical constants as noted in the preceding reference.

To determine the freezing-point depression of benzene on addition of phenol and its homologs the standard Beckmann apparatus and method were used. The thermometer was calibrated at the Bureau of Standards. Supercooling was limited to between 0.1° and 0.2°. For the depressions tabulated below the accuracy claimed is about 0.01°.

TABLE VII.  
FREEZING-POINT DEPRESSION DATA.

Phenol.									
Mol % Solute	0.97	1.81	3.17	4.50	6.38	7.92			
$\Delta T$ , °C.	0.398	0.711	1.190	1.621	2.221	2.635			
<i>o</i> -Cresol.									
Mol % Solute	0.88	1.86	2.84	3.81	4.71	5.95	7.53		
$\Delta T$ , °C.	0.591	1.170	1.752	2.257	2.728	3.341	4.082		
<i>m</i> -Cresol.									
Mol % Solute	0.67	1.54	2.00	3.10	4.33	5.43	6.01		
$\Delta T$ , °C.	0.439	0.925	1.161	1.711	2.161	2.584	2.843		
<i>p</i> -Cresol.									
Mol % Solute	0.95	2.01	3.18	4.54	5.70	7.10	8.68	10.33	
$\Delta T$ , °C.	0.590	1.180	1.691	2.225	2.625	3.102	3.569	4.065	
1 Phenol + 1 <i>o</i> -Cresol.									
Mol % Solute	1.15	2.33	3.64	5.07	6.65	7.79	9.46		
$\Delta T$ , °C.	0.602	1.180	1.774	2.383	2.998	3.444	4.060		
1 Phenol + 2 <i>m</i> -Cresol.									
Mol % Solute	0.66	1.71	2.78	4.04	5.70	7.25	8.70	10.24	11.74
$\Delta T$ , °C.	0.380	0.908	1.396	1.905	2.490	2.987	3.409	3.890	4.347
1 <i>o</i> -Cresol + 2 <i>p</i> -Cresol.									
Mol % Solute	0.91	2.02	3.02	4.11	5.34	6.72	8.59		
$\Delta T$ , °C.	0.590	1.218	1.727	2.239	2.743	3.275	3.953		

The positions of three of the resultant freezing-point depression curves (those for phenol, for *o*-cresol, and for an equimolecular mixture of phenol and *o*-cresol) with respect to the ideal are shown in Fig. 3. Phenol is evidently far from being monomolecular in benzene solution, the abnormally small depressions obtained pointing towards very extensive association. The curve for *o*-cresol, on the other hand, is very much closer to the ideal curve, indicating that this substance is far less highly associated in benzene solution.<sup>28</sup> The equimolecular mixture, finally, gives

<sup>29</sup> Hildebrand, (THIS JOURNAL, 38, 1452 (1916)) has shown that it is dangerous to ascribe deviations from the ideal curve to differences in molecular complexity when the solutes possess very divergent internal pressures. In view of the essential similarity in character of phenol and the cresols, however, the comparisons here made between

a curve which falls almost exactly midway between those of its two components. In other words, the average molecular complexity is practically unchanged by admixture.

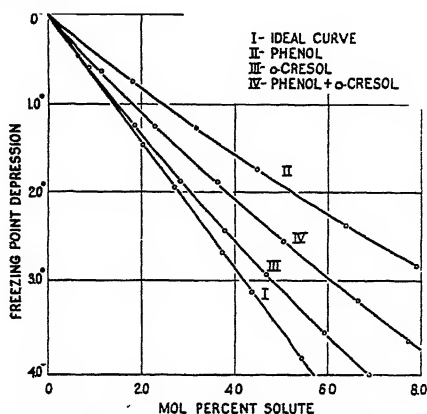


Fig. 3.—Freezing-point depression curves in benzene.

Precisely the same behavior is exhibited by the remaining results presented in Table VII (p. 1862). Each of the two mixtures tested (phenol and *m*-cresol in molecular proportions 1 to 2; *o*-cresol and *p*-cresol in the molecular proportions 1 to 2) corresponds to a definite compound isolated by Dawson and Mountford. The freezing-point depression curve in each case is found to occupy a position intermediate between the curves of the respective components, and nearer to that component which is present in excess.

If these phenol-cresol compounds were true *addition compounds* (their formation involving an increase in molecular complexity) entirely different results would have been obtained. Even although dissociation of such compounds into their simpler components would be greatly favored by the dilution of the mixture with a large excess of solvent benzene, we should still find appreciable combination indicated by abnormally small freezing-point depressions. Thus, to cite an instance, which will be taken up in detail in a subsequent communication, the freezing point of a solution of ethyl acetate in benzene is practically unchanged on addition of an equimolecular amount of trichloro-acetic acid,<sup>29</sup> showing that the acid-ester addition compound formed is only very slightly broken up into its components in benzene solution. A similar, but much less decided in their association factors are valid, even although the absolute values, as given later, may not be altogether correct.

<sup>29</sup> In a previous article (Kendall and Booge, *THIS JOURNAL*, 38, 1712 (1916)) it has been shown that these two substances form a stable equimolecular addition compound, melting at  $-27.5^{\circ}$ .

crease in molecular complexity on admixture in benzene solution is exhibited by ethyl acetate and acetic acid. In the cases here studied, however, the freezing-point depression curves resemble the viscosity curves in indicating that hardly any change in average molecular complexity occurs in phenol-cresol mixtures; any compound formation between the components must therefore be compensated for by simultaneous depolymerization

In order to obtain a definite idea with regard to the relative molecular complexities in the different solutions examined in this article, the following table may be consulted. As an arbitrary fixed concentration for comparing the various systems, 5 mol % solute has been selected. Specific-conductivity and viscosity data are added for convenience of reference in the subsequent discussion.

TABLE VIII.  
ASSOCIATION OF PHENOL, ETC., IN BENZENE SOLUTION.  
(Solute concentration = 5 mol %.)

	$\Delta T$ .	Mol. Wt.	Average mol. complexity.	Spec. cond. $\times 10^8$ , 25°.	Viscosity 25°.
Phenol .....	1.780	178.4	1.897	8.84	0.08945
<i>o</i> -Cresol .....	2.861	125.1	1.157	0.127	0.07608
<i>m</i> -Cresol .....	2.450	146.9	1.358	1.397	0.1342
<i>p</i> -Cresol .....	2.400	150.2	1.390	1.378	0.1474
1 Phenol + 1 <i>o</i> -Cresol	2.342	144.5	1.427	0.979	0.08415
1 Phenol + 2 <i>m</i> -Cresol	2.258	153.2	1.482	2.230	0.1121
1 <i>o</i> -Cresol + 2 <i>p</i> -Cresol	2.613	137.6	1.274	0.570	0.1177

The results are in good agreement with those of previous investigators<sup>30</sup> in indicating that phenol is much more highly associated than the cresols. The specific conductivity of phenol, it will be noted, is also considerably greater than the values obtained for the cresols, a point in exact accordance with the work of Kendall and Gross<sup>31</sup> in which a parallelism between specific conductivity and molecular complexity in a series of liquids of similar type was predicted.

*o*-Cresol is much less associated than its two isomers, all of the physical properties of which are strikingly similar. In line with this, the specific conductivities of *m*-cresol and *p*-cresol are much higher than that for *o*-cresol. The influence of a larger association factor is also evident in the relative viscosity values.

With regard to the behavior of the three binary mixtures tested, nothing needs to be added here to what has been said in the discussion above.

<sup>30</sup> Beckmann, *Z. physik. Chem.*, **2**, 725 (1888); Auwers, *ibid.*, **12**, 689 (1893); Mascarelli and Benati, *Gazz. chim. ital.*, [2] **37**, 527 (1907); [2] **39**, 642 (1909); Hewitt and Winmill, *J. Chem. Soc.*, **91**, 441 (1907).

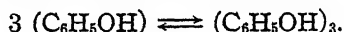
<sup>31</sup> Kendall and Gross, *THIS JOURNAL*, **43**, 1418 (1921).

### General Conclusions.

The following experimental facts have been established with regard to phenol-cresol mixtures: (a) 5 out of 6 of the possible binary systems give isolable compounds by the freezing-point method; (b) no significant changes in specific conductivity occur on admixture in any case; (c) the viscosity-composition curves are all "pseudo-ideal" in type; (d) the freezing-point depression curves given by binary mixtures in benzene solution are intermediate between the curves found for the pure components. The conclusions drawn from these several facts are not all in harmony with one another, as has been remarked upon at various places in the text above. It remains for us to examine whether a rational reconciliation can be effected now between the various results and the general hypothesis correlating chemical contrast, compound formation and conductivity in solutions developed in previous articles of this series, or whether the whole behavior of systems containing phenols must continue to be classed as "abnormal."

On careful consideration of the problem, it appears that an extension to these solutions of the views presented by Kendall and Gross<sup>32</sup> regarding conductivity and molecular complexity in pure associated liquids and in binary mixtures of the same supplies a complete explanation of all the points in dispute.

Phenol and its homologs, as already shown, are highly associated in the liquid state. The association of phenol, in particular, has been critically investigated by Yamanoto,<sup>33</sup> the conclusion reached being that the main equilibrium is represented by the equation,



Determinations of the molecular weight of phenol in various organic solvents by other workers, however, indicate that still more complex molecular types are also existent. The attractive forces between simple molecules, inducing the formation of larger molecular aggregates in the liquid, must consequently be very pronounced; in other words, the substance is markedly "polar." The same applies, to somewhat less degree, to the three cresols.

Now it has been noted by Kendall and Gross that in a solution containing two highly associated components of similar character, compounds of the general type  $(\text{AB})_x(\text{CD})_y$  are undoubtedly formed in quantity. The average molecular complexity of such a mixture, however, (and hence its specific conductivity also) will not differ greatly from that of its pure components, since extensive disassociation of these is also involved. The complexes here existent are to be regarded, indeed, not as *addition* but

<sup>32</sup> Kendall and Gross, *THIS JOURNAL*, 43, 1420 (1921).

<sup>33</sup> Yamanoto, *Sakurai Memorial Papers*, No. 12, p. 33 (1908).

rather as *substitution* compounds, for disintegration and recombination of the various molecular and ionic types present will evidently result, finally, in an almost "haphazard" replacement of the different radicals by one another at all points of the original associated molecules. If the attractive forces between the constituent groups are such that a certain particular substitution complex predominates in stability, then it is only logical to expect that such a complex may be definitely isolated under suitable conditions. (*e. g.*, by freezing the solution.) The phenol-cresol compounds discovered by Dawson and Mountford are consequently not true addition compounds (as, indeed, the physical properties investigated in this article have sufficiently demonstrated) but substitution compounds formed by the replacement of part of an associated molecule by a homolog. It is very significant in this connection that *all* of the five compounds isolated by Dawson and Mountford are trimolecular, *e. g.*, 1 phenol + 2 *m*-cresol. Such complexes could evidently be readily formed from the predominating phenol complex  $(C_6H_5OH)_3$  by replacement of two phenol groups. No increase in the average molecular complexity of the mixture is involved in such replacements, and the apparent contradiction between Dawson and Mountford's results and those of the present work is therefore entirely removed.

It must also be noted that mixtures of this type, if no particular substitution complex predominates in stability, will necessarily tend to give "mixed crystals" on solidification. This is here the case with one system only, phenol:*o*-cresol. A careful determination of the solidus curves would indicate, in all probability, limited formation of solid solutions in the remaining systems. Precisely analogous behavior is shown by binary mixtures of fused salts of similar character, *e. g.*, neutral salts of the alkali metals.<sup>34</sup> Thus potassium sulfate gives a continuous series of solid solutions with sodium sulfate and with potassium chromate. Lithium sulfate and potassium fluoride, on the other hand, form stable equimolecular compounds with potassium sulfate. These latter systems are evidently identical in character with the five compound-producing phenol-cresol mixtures here examined.

### Summary.

By repeated fractionation, very pure samples of phenol and the three cresols have been prepared, and their chief physical constants determined. The specific conductivity and viscosity curves for phenol-cresol mixtures have been carefully investigated; freezing-point depression curves for phenol, the cresols, and various binary mixtures in benzene solution have also been constructed. Without exception, the results indicate that no increase in molecular complexity occurs on admixture. This is in agree-

<sup>34</sup> Landolt-Börnstein, "Tabellen," 1912, p. 611-87.



ment with the views correlating addition compound formation with diversity in character of the components developed in previous articles of this series. It is apparently in disagreement, however, with the fact that Dawson and Mountford succeeded in isolating definite compounds from phenol-cresol mixtures in five out of six systems.

A brief consideration of the equilibria existent in binary mixtures of associated liquids has shown that the compounds obtained by Dawson and Mountford are to be regarded as substitution rather than as addition compounds. Under this view, no conflict exists between the results of Dawson and Mountford and those of the present work; both fall directly into line with the general theory.

NEW YORK, N. Y.

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## SOME PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS OF CERTAIN PYRIDINE BASES.

BY WILLIAM JACOB JONES AND JOHN BAMBER SPEAKMAN.

Received June 8, 1921.

The physical properties of mixtures of pyridine and water have been the subject of a number of investigations.<sup>1</sup> The optical and thermal constants of pyridine and the mono methylpyridines have been determined by Constam and White.<sup>2</sup> More aqueous solutions of the higher homologs of pyridine have not been examined up to the present with the exception of 3 and 4 methylpyridines and 2,6-dimethylpyridine, studied by Flaschner.<sup>3</sup> In the present article are given measurements of densities and other physical characteristics of aqueous solutions of some of these higher homologs.

### Preparation of Materials.

The bases used had been purified by the methods described elsewhere.<sup>4</sup> On account of their hygroscopicity they were redistilled before use from solid sodium hydroxide, in an apparatus previously dried by the passage of air dried with sulfuric acid, and the receiver was protected from the external air by a calcium chloride tube. They were then preserved in desiccators kept in the dark. The aqueous solutions were made up by weight with conductivity water in the type of weighing bottle recommended by Hartley, Thomas and Applebey, having its stopper fitting over the outside of the neck.

<sup>1</sup> "Absorption by Electric Waves," Bredig, *Z. Elektrochem.* 7, 767 (1901); "Densities and Viscosities," Dunstan, Thole and Hunt, *J. Chem. Soc.*, 91, 1718 (1907); "Densities, Viscosities and Surface Tensions," Hartley, Thomas and Applebey, *ibid.*, 93, 538 (1908); "Refractive Indices and Partial Vapor Pressures," Zawidski, *Z. physik. chem.*, 35, 129 (1900), "Composition of Constant Boiling Mixtures," Goldschmidt and Constam, *Ber.* 16, 2977 (1883).

<sup>2</sup> Constam and White, *Am. Chem. J.*, 29, 1 (1903).

<sup>3</sup> Flaschner, *J. Chem. Soc.*, 95, 668 (1909).

<sup>4</sup> Heap and Jones, *THIS JOURNAL*, 43, 1936 (1921).

## Densities.

It was originally intended to employ the determinations of the densities of aqueous solutions of pyridine made by Hartley, Thomas and Applebey,<sup>1</sup> for the purpose of finding the composition of the constant-boiling mixture. Since a different value for the density of anhydrous pyridine was found, it was necessary for our needs to redetermine the densities. Freshly distilled samples were used. Our values are corrected for air displacement and are here tabulated. The table also embodies the results obtained by us for 2- and 3-methylpyridines.

TABLE I.  
DENSITIES.

Water. %	Pyridine. $d_4^{20}$	2-Methylpyridine. $d_4^{20}$	3-Methylpyridine. $d_4^{20}$
0	0.9776	0.9404	0.9515
10	0.9888	0.9637	0.9675
20	0.9979	0.9787	0.9778
30	1.0018	0.9867	0.9845
40	1.0028	0.9911	0.9881
50	1.0032	0.9936	0.9905
60	1.0029	0.9952	0.9924
70	1.0020	0.9960	0.9938
80	1.0008	0.9965	0.9950
90	0.9991	0.9968	0.9962
100	0.9971	0.9971	0.9971

## Compositions of the Constant-boiling Mixtures.

Goldschmidt and Constam<sup>1</sup> who were the first to prepare the constant-boiling mixture in the case of aqueous pyridine, concluded that it was an undissociated compound,  $C_5H_5N \cdot 3H_2O$ , basing their conclusions on its nitrogen content and its vapor density, which they gave as 1.19 to 1.16, referred to air. This value of the vapor density, however, corresponds with complete dissociation, and the accuracy of the value given by them is borne out by our experiments, in which the Victor Meyer method was used. The vapor density of the constant-boiling mixture of 2-methylpyridine and water also corresponds with complete dissociation.

We have also undertaken determinations by the cryoscopic method of the molecular weights of the bases in aqueous solution. For this purpose we prepared standard aqueous solutions of pyridine and of 2-methylpyridine by adding known weights of the constant-boiling mixtures to known weights of water. In solutions containing less than 4% of the bases the molecular weights obtained are those of the bases, namely, 79 and 93 respectively. With 6% solutions our results indicate that, if it may be assumed that we are still dealing with dilute solutions, either there is polymerization of the base, which is improbable, or there is partial conversion into hydrate.

# Variation of the Composition of the Constant-boiling Mixtures with Pressure.

The method of investigation here employed was that of Roscoe.<sup>5</sup> Our results were as follows:

TABLE II.  
VARIATION OF COMPOSITION OF CONSTANT-BOILING MIXTURES WITH THE PRESSURE.

Pressure. Mm. Hg.	Boiling point. °C.	Density of distillation. $d_4^{25}$
Pyridine.		
767.0	93.0	1.00315
633.5	87.7	1.00313
483.0	80.8	1.00311
358.5	73.7	1.00316
235.5	64.2	1.00316
2-Methylpyridine.		
753.0	93.5	0.99318
653.0	89.5	0.99318
572.5	86.4	0.99318
401.5	77.5	0.99318
194.0	61.5	0.99320
3-Methylpyridine.		
768.0	96.2	0.99247
596.0	89.6	0.99255
450.0	82.2	.....
425.5	80.8	0.99259
270.0	70.0	0.99276

From these results we deduce that the variation in density is slight but real. Therefore, in view of our vapor-density results and of this fact, we can state definitely that these constant-boiling distillates are mixtures and not compounds.

Making use of our density data we find that the constant-boiling mixture of water with pyridine contains 42% of water; with 2-methylpyridine, 48% of water; and with 3-methylpyridine, 61% of water. In the case of 2-methylpyridine this corresponds with the formula  $4\text{C}_6\text{H}_7\text{N} \cdot 19\text{H}_2\text{O}$ , and in the case of 3-methylpyridine, with  $3\text{C}_6\text{H}_7\text{N} \cdot 25\text{H}_2\text{O}$ , which is further confirmation of the non-existence of compounds.

TABLE III.

MISCIBILITY OF 2,4-DIMETHYLPYRIDINE<sup>6</sup> WITH WATER.

Water, % by Wt.	15.99	23.14	30.92	37.50	45.14	55.11	67.96	79.54	93.00	95.06
Lower solution point, °C.....	>150	>150	68.5	53.0	39.0	27.2	23.0	23.0	35.0	54.3

The minimum critical solution temperature is 22.5°. The composition of the constant-boiling mixture of 2,4-dimethylpyridine and water

<sup>5</sup> Roscoe, *J. Chem. Soc.*, 13, 146 (1861); 15, 270 (1862).

<sup>6</sup> The solubility of this base in water was determined by Alexéeff's method.

was determined by means of the solubility curve. A mixture of 2,4-dimethylpyridine and water was distilled, and the distillate which boiled constantly at  $96.5^{\circ}$  consisted of two layers. When the distillate was cooled below  $23.2^{\circ}$ , it became homogeneous. Reference to the miscibility data showed that it contained 66% of water.

### Summary.

The densities of aqueous solutions of pyridine, 2-methylpyridine and 3-methylpyridine have been determined. The compositions of the constant-boiling mixtures have also been ascertained, and found to be 42%, 48% and 61% of water respectively. Solubility data for 2,4-dimethylpyridine have also been given.

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## A THEORY OF ALLOTROPY.

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Received November 18, 1920.

The term *allotropy* was first introduced by Berzelius,<sup>1</sup> as denoting the appearance of an element in several states distinguished from one another by different properties, a definition lacking in precision, owing to the numerous possible interpretations of the "different properties."

Allotropy is taken as a term covering the different physical states of matter, and also isomerism, polymerism and polymorphism,<sup>2</sup> and in this sense might appear, perhaps, to be an unnecessary term without exact meaning in chemical nomenclature.

This inclusion of different phenomena, along with Ostwald's and Nernst's definition of allotropy on the basis of energy changes, and Benedick's, Honda's and Le Chatelier's conception based upon the discontinuity of forms, phases and properties, is due to the consideration of *effects* of, instead of *causes* underlying phenomena.

While a close study of the various properties of matter consequent to a certain phenomenon may help us in comprehending the phenomenon itself and its relationship to other natural manifestations, it is wrong to define a phenomenon by its effects, especially when these effects are anything but specific or characteristic. A far truer and more productive definition would be based upon the study of the *causes* of a phenomenon, the unmasking of which should naturally throw much light upon the phenomenon itself and its probable effects.

The possible causes of allotropy may be either (a) a variation in the intramolecular structure of elements, or (b) a change in the intermolecular association or aggregation of elements.

<sup>1</sup> Berzelius, *Jahresber.* 20, [II] 13 (1841).

<sup>2</sup> Lehmann, *Z. Kryst. Min.*, 1, 97 (1877); Lowry, *Trans. Faraday.*, 11, 150 (1916).

Considering that (1) molecular aggregation subject to the laws of crystallography accounts for polymorphism,<sup>3</sup> and that (2) allotropic modifications present in most cases considerable chemical and physical differences, it would appear that allotropy is due to intramolecular differences.<sup>4</sup> We can regard allotropy not only as a function of valence, but also define it as the capacity of an element to exist in forms differing in the mode of their intramolecular linkage.

The conception of valence adopted by the author is that represented by the "primary valence" of Abegg and Werner.

This conception of allotropy is in full accord with (a) the hypothesis of dynamic allotropy,<sup>5</sup> as on this basis only a simple space lattice, revealed by the reflection of X-rays from the internal planes of crystals, can be deduced; and (b) the *view* of different ions existing in solution in presence of two allotropes of an element.<sup>6</sup>

In this sense allotropy, although a function of valence, does not imply isomerism or polymerism, as allotropes need not necessarily contain the same or a multiple number of atoms in their respective molecules. This conception of allotropy can be clearly understood on the basis of the electronic theory. According to this theory the valence bonds are considered as having a definite direction. The relative direction of these bonds in the molecule may be influenced by the conditions under which such a molecule is formed. Variation in the direction would give rise to molecular structures differing in the distribution of electric charges among the constituent atoms. These would be allotropes, and that configuration in which the charges were most symmetrically arranged or neutralized would be the stable form under these conditions.

Recognizing allotropy as a function of valence and knowing the valence of an element (the maximum one in case of elements of variable valence), we should be able to indicate not only the possible constitutional formulas of allotropes, but also the maximum number of allotropes possible for each individual element. Studying the possible constitutional formulas for molecules of elements on the basis of their valences we find that the problem resolves itself into the definition of the number of possible conditions or modes of freedom of an atom of the element in question.

I. An atom of the monoatomic *inert* gases can exist in *one* condition only.

<sup>3</sup> Wyroubow, *Bull. sos. min.*, **26**, 335 (1906).

<sup>4</sup> Blanshard, *Chem. News*, **70**, 295 (1894).

Köppel, *Naturw. Rund.*, **19**, 249, 261 (1904).

Guthrie, *J. Roy. Soc. N. S. Wales*, **14**, 318 (1911).

Oxley, *Trans. Faraday Soc.*, **11**, 129 (1916).

<sup>5</sup> Smits, *Verslag. Akad. Wetenschappen Amsterdam*, 19101-920.

<sup>6</sup> Holt, *J. Soc. Chem. Ind.*, **34**, 693 (1915).

II. An atom of a *monovalent* element can exist in *two* conditions only: (a) fixed valence,  $\cdot\text{---}$ ; (b) free valence,  $\cdot\text{---}$ . Halogens at high temperature and probably nascent hydrogen are cases of monovalent elements containing a free valence.

III. An atom of a *divalent* element may exist in *two* conditions only: (a) fixed valence,  $\cdot\text{---}$ ; (b) free valence,  $\text{---}\cdot\text{---}\cdot\text{---}$  or valences,  $\text{---}\cdot\text{---}$

IV. An atom of a *trivalent* element may exist in *two* forms only: (a) a saturated state with no free valences,  $\cdot\text{---}\cdot\text{---}\cdot\text{---}$ ; (b) an unsaturated condition with free valences,  $\cdot\text{---}$ ,  $\cdot\text{---}\cdot\text{---}$ ,  $\cdot\text{---}\cdot\text{---}\cdot\text{---}$ .

V. An atom of a tetra-, penta- or other polyvalent element may exist in *three* forms or conditions only: (a) a saturated condition, in which the atom is rigidly fixed,  $\cdot\text{---}\cdot\text{---}\cdot\text{---}\cdot\text{---}$ ,  $\cdot\text{---}\cdot\text{---}\cdot\text{---}\cdot\text{---}$ ; (b) an unsaturated condition, in which the atom is rigidly fixed by having three or more of its valences fixed,



(c) an unsaturated condition, in which the atom is not rigidly fixed,  $\text{---}\cdot\text{---}$ ,  $\cdot\text{---}\cdot\text{---}\cdot\text{---}$ ,  $\cdot\text{---}\cdot\text{---}\cdot\text{---}\cdot\text{---}$ .

It appears that while a polyvalent atom linked to one or two other atoms has the power of free rotation (the valences being regarded as axes, representing polar forces, the axis of rotation may not be common to any valence, but represented by the resolved effect of all valences concerned), an atom linked to 3 or more atoms has no such power of rotation, and can be regarded as rigidly fixed. As atoms of each condition can form by their combination with one another one and only one distinct molecular form, and as a combination of atoms, individually in different states, is most improbable, we are justified in concluding the maximum number of allotropic modifications of an element under the most favorable conditions of temperature and pressure (forms not necessarily occurring in *all* physical states) to be as follows: (1) the inert gases may exist in *one* form only; (2) the mono-, di-, and trivalent elements may exist in *two* forms only; and (3) the tetra-, penta- and other polyvalent elements may exist in not more than *three* distinct intramolecular forms.

While the valence of an element determines the number of possible allotropes, comparative examination of the chemical and physical properties of any element in all its forms should enable us to define with fair precision the intramolecular structure of each allotrope.

A scrutiny of the possible molecular forms of elements shows that theoretically it is possible for an element to have in certain cases more than one molecular form corresponding to each mode of linkage indicated above; that is, there may occur more than one form of an element with a rigid or non-rigid configuration. But regarding allotropes as the most chemically and physically distinct forms of an element it is obvious that several molecular forms, each containing a different number of atoms, but all having the power of free rotation, will differ among themselves to a less extent than when compared with a molecular structure of the same element, in which all atoms are rigidly fixed. Thus it follows that valence and the saturation or fixation of the atoms, and not the actual number of atoms, play the predominant part in the determination of allotropes. In this light allotropy becomes the capacity of an element to exist in forms differing in the mode of their intramolecular linkage. Molecular forms differing in the number of atoms or distribution of linkages, but all belonging to one and the same type of mode of linkage indicated above can be termed *allotropoids*. These molecular forms serve as a transition or link between polymorphism and allotropy proper. Each modification of an element, which is an allotropoid in relation to forms belonging to the same mode of linkage, is an allotrope when viewed in connection with modifications belonging to a different type of linkage. Allotropoids differ among themselves less in physical, and still less in chemical properties than allotropes of the same element.

The problem of discriminating between allotropy and polymorphism or intra- and inter-molecular structures,—comparatively easily solvable in the case of a few advanced characteristic instances, becomes therefore complicated and the available methods uncertain, not only owing to the inert character of some elements, which compels us to draw conclusions from their physical properties only, but also owing to the fact that in some cases we may deal with substances which are simultaneously either (1) allotropes and polymorphic forms, or (2) allotropoids and polymorphic forms. Thus the physical data may indicate the combined effect of intra- and inter-molecular rearrangements in the element; and as the components, the combination of which gives us the total effect, need not necessarily be magnitudes in the same direction, the physical data lose much of their comparative value.

The knowledge of the maximum possible number of allotropes, serving as a guiding limitation, augmented by the chemical and physical properties of the modifications, should be sufficient in most cases in identifying the

allotropes of an element. In cases where owing to the inertness of an element we have to depend upon the physical factor only, as many physical properties as possible are to be taken into consideration, since no single feature or property is sufficiently characteristic to serve as a decisive indication of allotropy. The functional connection of physical constants with the periodic system of atomic weights and volumes of elements make it very necessary, if any generalizations are to be made, to have the experimental conditions for the determination of physical constants specific for every element with special relation to the absolute melting and transition points of every modification of an element.<sup>7</sup>

Differences in crystalline symmetry are indefinite as a criterion or definition of allotropy, owing to the possibility of substances belonging either to different crystalline systems or different classes of the same system. The observation that the higher the crystalline symmetry of an element the smaller is the number of atoms constituting its molecule,<sup>8</sup> and consequently the smaller is its tendency to allotropy<sup>9</sup> is of an empirical character, and can hardly serve as a guiding principle in distinguishing allotropic from polymorphic forms, this being especially so as crystalline structures may depend at least as much upon molecular aggregation as on the intramolecular configuration of the atoms.

The sudden changes in the discontinuity of properties can be accepted as an indication of allotropy but with reserve, not only owing to the difficulty of establishing such discontinuity,<sup>10</sup> but also owing to the fact that such changes accompany both allotropy and polymorphism, and if there is any difference, it is in the degree, not the kind of change. The thermal changes so characteristic of the most pronounced allotropic transformations of the non-metallic elements, though often very useful as an indication, are not completely to be relied upon, as all thermal measurements for metals give decidedly lower values than for non-metals, and considerable changes of volume, hardness, porosity, electromotive forces, electrical resistance, specific heat, and the thermo-electric power are not necessarily accompanied by great heat changes. Considerable heat changes may be taken as a positive indication of allotropic rearrangement, but small heat changes are hardly safe as a negative proof, the more so as the heat evolution actually recorded may be the sum of two or more values of reactions, some exothermic and others endothermic.

As mentioned above, the allotropes of metals are more difficult to isolate and distinguish, than those of the non-metals. But even in cases

<sup>7</sup> Copisarow, *J. Inst. Metals*, **20**, 98 (1918).

<sup>8</sup> Retgers, *Z. physik. Chem.*, **14**, 1 (1894).

<sup>9</sup> Barlow and Pope, *J. Chem. Soc.*, **81**, 1741 (1906).

<sup>10</sup> Honda, *J. Iron Steel Inst.*, **91**, 199 (1915); *Science Repts. Tohoku Imp. Univ.*, [4] **3**, 261 (1915).



when no separate allotropic modifications have been isolated, (a) the dependence of such physical properties as density, specific heat, expansion, electrical conductivity, and the melting, solidification, and transition-points upon the thermal history of the specimen, and (b) the variation of the chemical behavior with the past history of the metal, are best explained on the basis of the allotropy hypothesis.

The constitutional formulas of allotropes developed on the basis of valence and the chemical and physical properties of each modification, although not actually solving the interesting problem of molecular complexity, offer us substantial aid in this respect, insofar as they often indicate the minimum molecular complexity satisfying the requirements of the formulas.

The consideration of the allotropy of elements, applying to elements mainly in their solid state, throws incidentally much light upon the general constitution of the solid state of matter.

The modern X-ray spectrometric investigations, though failing to indicate the display of forces between atoms, are showing the positions of atoms in space, thus affording a possible method of study of allotropes. Now as characteristic cases of allotropy we may discuss the allotropy of phosphorus, carbon, iron and nickel.

### Allotropy of Phosphorus.

The number of forms of phosphorus recorded from time to time in the literature is considerable. In several instances, however, a difference in color, mode of fracture, size of particles or slight deviation in the specific gravity (regardless of impurities) was taken as a sufficient basis for the announcement of a new form of phosphorus.

In addition to the white (ordinary, colorless or yellow) and red phosphorus, the following are described as distinct modifications: (1) *black* phosphorus (Thénard<sup>11</sup>); (2) *red* phosphorus, soluble in alkalis (Schenck<sup>12</sup>); (3) *scarlet* (ruby-red) phosphorus (Troost and Hautefeuille<sup>13</sup>); (4) *dense-red* phosphorus (Bridgman<sup>14</sup>); (5) *violet* (metallic or crystalline) phosphorus (Hittorf<sup>15</sup>); (6) *black* phosphorus (Bridgman<sup>14</sup>). Thénard's black phosphorus was proved by Blondlot, Ritter and Gernez<sup>16</sup> to be ordinary red phosphorus, contaminated with mercury and arsenic. Schenck's soluble red phosphorus appears to be ordinary red phosphorus in a state

<sup>11</sup> Thénard, *Compt. rend.*, **95**, 409 (1882).

<sup>12</sup> Schenck, *Ber.*, **36**, 979, 4202 (1903).

<sup>13</sup> Troost and Hautefeuille, *Compt. rend.*, **78**, 748 (1874).

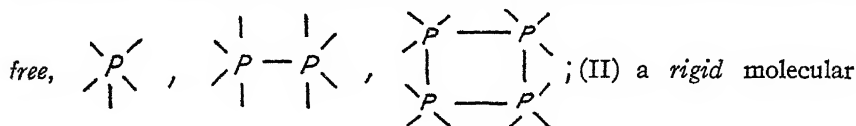
<sup>14</sup> Bridgman, *THIS JOURNAL*, **36**, 1344 (1914).

<sup>15</sup> Hittorf, *Pogg. Ann.*, **126**, 193 (1865).

<sup>16</sup> Blondlot, *Compt. rend.*, **70**, 856 (1870); **78**, 1130 (1874). Ritter, *ibid.*, **78**, 192 (1874). Gernez, *ibid.*, **151**, 12 (1910).

of fine division.<sup>17</sup> Troost and Hautefeuille's intensely colored form of phosphorus, as well as Bridgman's dense-red phosphorus, differing from red and Hittorf's violet modifications in no other property than color and a very slight deviation in specific gravity, must be regarded as belonging to one of the latter forms. Notwithstanding the considerable attention paid by investigators to ordinary red and Hittorf's violet phosphorus the question of their distinct character or individuality still remains unsettled.<sup>18</sup> But even assuming that red and violet phosphorus exist as two separate forms, we must admit that the very slight difference in physical properties, and the absence of any chemical differences make the contrast between red and violet phosphorus in no way as pronounced as that with either white or Bridgman's black modification. The character of the possible co-existence of red and violet phosphorus will be discussed at a later stage. Black phosphorus<sup>19</sup> must be regarded as a distinct modification of phosphorus, as it is characterized by its high density, conductivity of heat and electricity, low specific heat and vapor pressure, and general stability. Thus we find that phosphorus occurs in three chemically and physically distinct forms: (1) white, colorless or yellow; (2) red, and Hittorf's violet or metallic; and (3) black phosphorus.

Now on the basis of the theory of allotropy phosphorus, being pentavalent, may exist in *not more* than three chemically and physically distinct forms: (I) a *non-rigid* molecular form, in which *some* valences are



form, *some* valences of which are *free* (Fig. 1, tetrahedron); (III) a *rigid* molecular form, *all* valences of which are *fixed* (Fig. 2, icosahedron).

It is clear from the three constitutional formulas that a molecule represented by non-rigid configuration (Class I) will be characterized by comparative reactivity, small specific gravity, high vapor pressure, low melting point, etc.

A molecule represented by a rigid configuration (Class III) will exhibit properties exactly opposite to those just indicated, while the molecular structure, Class II, will be intermediate in all its properties. Comparing

<sup>17</sup> Pedler, *J. Chem. Soc.*, **57**, 599 (1890).

<sup>18</sup> Wegscheider and Kaufer, *Monatsh.*, **22**, 700 (1901).

Linck and Möller, *Ber.*, **41**, 1404 (1908).

Jolibois, *Compt. rend.*, **151**, 382 (1910).

Stock, Schrader and Stamm, *Ber.*, **45**, 1514 (1912).

<sup>19</sup> Bridgman, *THIS JOURNAL*, **38**, 609 (1916).

Smits, Meyer and Black, *Verslag Akad. Wetenschappen Amsterdam*, **18**, 992 (1916).

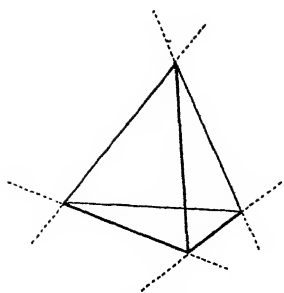


Fig. 1.

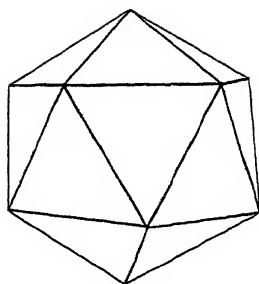


Fig. 2.

the physical and chemical properties of white, red (violet) and black phosphorus with those which we may expect to accompany certain molec-

Form of Phosphorus.	Vapor Press. (400–447°) Mm. of Hg.	Sp. Gravity.
White .....	570.	1.83
Black .....	58.5	2.691
Red. i. ordinary .....	164.0	} 2.05 to 2.34
ii. Troost and Hautefeuille .....	133.0	
iii. Bridgman .....	73.2	
iv. violet .....	93.0	

ular configurations, we find no difficulty in assigning to each distinct form of phosphorus its constitution formula, *viz.*, white, Class I; red, Class II; and black, Class III.

The following considerations show not only the existence of a striking agreement between the theory of allotropy and the deductions based upon it, and the experimental facts, but also the remarkable way in which this theory elucidates and consolidates isolated and uninterpreted facts.

1. Class I may be taken as a just representation of the constitution of both white phosphorus and phosphorus vapor since the molecular complexity of white phosphorus,<sup>20</sup> as well as that of phosphorus vapor<sup>21</sup> is represented by  $P_4$  and the transition of white phosphorus to vapor is reversible.<sup>21</sup>

2. A regular tetrahedron ( $P_4$ ), is a correct representation of the molecular constitution of red phosphorus, as (a) the vapors of white, red and black phosphorus are identical; (b) the transition from red phosphorus

<sup>20</sup> Schenck, *Ber.*, **35**, 351 (1902).

Stock, Gibson and Stamm, *ibid.*, **45**, 3527 (1912).

<sup>21</sup> Mitscherlich, *Ann.*, **12**, 137 (1834).

Deville and Troost, *Compt. rend.*, **56**, 891 (1863).

Paterno and Nasini, *Ber.*, **21**, 2153 (1888).

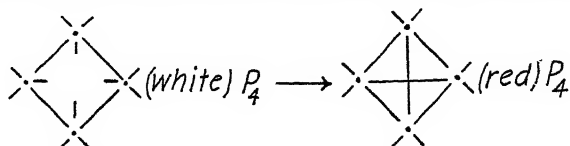
Hertz, *Z. physik. Chem.*, **6**, 358 (1890).

Beckmann, *ibid.*, **5**, 76 (1890).

Chapman, *J. Chem. Soc.*, **75**, 735 (1899).

to vapor is irreversible; and (c) the transformation of white to red phosphorus is a monomolecular reaction.<sup>22</sup>

The transformation of white to red phosphorus is represented by the passage from a *plane* configuration to a *three-dimensional* structure.

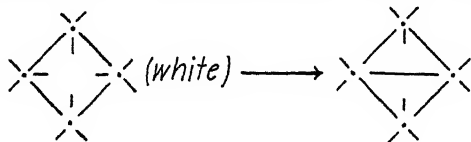


3. A close examination of the constitution formulas deduced above for white, red and black phosphorus offers us a clear explanation of the fact observed by Bridgman,<sup>19</sup> *i. e.*, the transformation of white phosphorus to black, and the failure of red (or violet) to undergo such a change.

No polymerization unaccompanied by a complete disruption of the molecule can transform a molecular structure represented by a tetrahedron (red phosphorus) into one represented by a regular icosahedron (black phosphorus). On the other hand the transformation of white phosphorus to black is constitutionally a simple polymerization closely resembling the acetylene  $\rightarrow$  benzene transformation, *viz.*,  $3 P_4 = P_{12}$ .

Following up this polymerization we see that there is a probability of an intermediate stage or form between white and black phosphorus.

The *plane* configuration of white phosphorus probably passes at 200° and 11000–12000 kg./cm<sup>2</sup>. pressure, through an asymmetric, apparently unstable, *two-plane* form, before polymerizing to black phosphorus.



This consideration is in remarkable agreement with Bridgman's observation of a preliminary reaction, a "preparation-period" in the transformation of white to black phosphorus.

The question of violet phosphorus, as previously indicated, is still unsettled; but even assuming that violet phosphorus is a distinct form, such an assumption would in no way undermine the validity of the theory of allotropy.

As indicated in the theory of allotropy in case of polyvalent elements more than one molecular form, belonging to the same type of configuration, is possible, *i. e.*, molecular forms differing in the number of atoms, without any radical difference in the mode of linkage. Thus a molecular con-

<sup>22</sup> Schenck, *Ber.*, 36, 4202 (1903).

figuration,  $P_8$ , represented by a cube (see Fig. 3) would offer a satisfactory conception of the constitution of violet phosphorus, as such representation similar to Fig. 1 assigned to red phosphorus would be a *rigid* form, containing *free* valences. A molecular form of such constitution, a direct product of polymerization of white phosphorus by the condensation of two molecules, would be quite tangible, as the conditions of transformation of white to violet are more drastic than those of white to red phosphorus.

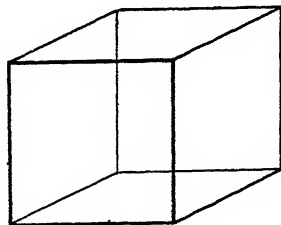


Fig. 3.

Therefore, should the separate existence of red and violet phosphorus be established, they will have to be regarded as *allotropoids* in relation to each other, and as *allotropes* in relation to *white* and *black* phosphorus.  $P_1$  and  $P_2$ , the high temperature dissociation products of phosphorus vapor,<sup>23</sup> belonging qualitatively to the molecular structure represented by by Class I are hence *allotropoids* in relation to the vapor  $P_4$  and white phosphorus, and *allotropes* in relation to red (violet) and black phosphorus.

### Allotropy of Carbon.

In the light of the chemistry of carbon compounds a carbon atom can be regarded as always potentially tetravalent. The polyatomicity of a carbon molecule is proved by (1) the existence of several distinct forms of carbon; (2) the high volatilization point of carbon; (3) the products of moist oxidation; (4) the combustion of carbon;<sup>24</sup> (5) the X-ray spectroscopic study of the modifications of carbon.<sup>25</sup> Attempts have been made to study the complexity of carbon molecules and to establish the constitutional molecular formulas of one or more forms of carbon by Kekulé,<sup>26</sup> Vaubel,<sup>27</sup> Barlow and Pope,<sup>28</sup> Dewar,<sup>29</sup> Aschan,<sup>30</sup> Dimroth and Kerkovius,<sup>31</sup> Bragg,<sup>32</sup> Meyer,<sup>33</sup> and Debye and Scherrer.<sup>25</sup>

Reviewing these investigations we find that a method of study so general as to be applicable to all forms of carbon has not yet been proposed.

<sup>23</sup> Preuner and Brockmöller, *Z. physik. Chem.*, **18**, 129 (1913).

Stock and Stamm, *Ber.*, **46**, 3497 (1913).

<sup>24</sup> Rhead and Wheeler, *J. Chem. Soc.*, **97**, 2181 (1910); **99**, 1140 (1911); **103**, 461 (1913).

<sup>25</sup> Debye and Scherrer, *Physik. Z.*, **17**, 277 (1916); **18**, 291 (1917).

Olie and Byl, *Verslag Akad. Wetenschappen Amsterdam*, **19**, 920 (1917).

<sup>26</sup> Kekulé, *Z. angew. Chem.*, **12**, 950 (1899).

<sup>27</sup> Vaubel, *ibid.*, **13**, 60 (1900).

<sup>28</sup> Barlow and Pope, *J. Chem. Soc.*, **89**, 1742 (1906).

<sup>29</sup> Dewar, *Chem. News*, **97**, 16 (1908).

<sup>30</sup> Aschan, *Chem. Ztg.*, **33**, 561 (1909).

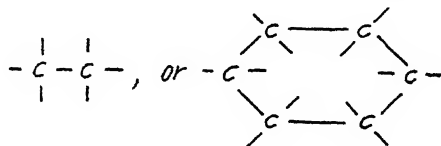
<sup>31</sup> Dimroth and Kerkovius, *Ann.*, **399**, 120 (1913).

<sup>32</sup> Bragg, *Proc. Roy. Soc.*, **89A**, 280 (1913).

<sup>33</sup> Meyer, *Monatsh.*, **35**, 163 (1914).

While the method of moist oxidation can be applied more or less successfully to amorphous carbon and to some extent to graphite, the X-ray method is confined to diamond with a somewhat strained extension to graphite.

Now if we consider the problem from the point of view of valence, *i. e.*, molecular structure, we secure at once a general method of investigation. In the light of the theory of allotropy, carbon having a valence greater than three may exist in three distinct molecular forms: (I) a *non-rigid*



molecular configuration, some valences of which are *free* (see also Fig. 4); (II) a *rigid* molecular configuration, some valences of which are *free* (see Fig. 5); and (III) a *rigid* molecular configuration, all valences of which are fixed (see Fig. 6).

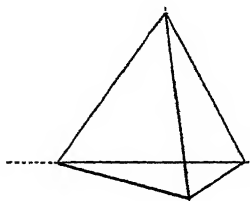


Fig. 4.

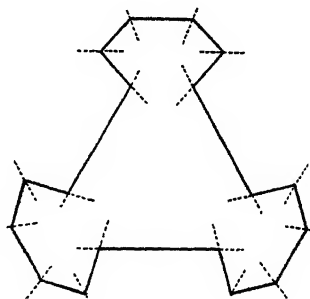


Fig. 5.

The several new modifications of carbon (graphitoid, graphitite, etc.) suggested by Brodie, Berthelot, Luzi and others have been proved to be either compounds, solutions or mixtures of carbon with some other elements.<sup>34</sup>

<sup>34</sup> Porcher, *Chem. News*, **44**, 203 (1881).

Bartoli and Papasogli, *Gazz. chim. ital.*, **12**, 113 (1882); **13**, 37 (1883); **15**, 445 (1885).

Moissan, *Compt. rend.*, **116**, 609 (1883); **119**, 976 (1894); **120**, 17 (1895); **121**, 540 (1895); *Ann. chim. phys.*, [VII] **8**, 289, 306, 466 (1896).

Wiesner, *Monatsh.*, **13**, 371 (1892).

Weinschenk, *Z. Kryst. Min.*, **28**, 291 (1897).

Hyde, *J. Soc. Chem. Ind.*, **23**, 300 (1904).

Trener, *Jahresber. Geol. Reichs. Wien.*, **1906**, 405; *Z. Kryst. Min.*, **46**, 124 (1909).

Charpy, *Compt. rend.*, **145**, 1173 (1907); **148**, 920 (1909).

Le Chatelier and Wologdine, *ibid.*, **146**, 49 (1908).

Debye and Scherrer's<sup>25</sup> experiments merely indicate the presence of graphite in amorphous carbon, and the absence of other crystalline forms. These experiments afford, however, no ground for the unification of graphite with amorphous carbon.

No matter how finely divided graphite may be (Acheson's or "colloidal" graphite), its behavior towards moist oxidants, its products of oxidation, mode of combustion and physical properties—all greatly differ from those of amorphous carbon.

Meyer<sup>33</sup> and Meyer and Steiner,<sup>35</sup> recording the dependence of the yield of mellitic acid from charcoal upon the latter's source and temperature of carbonization, express some doubt as to the entity of the carbon "molecule" and the close connection of its constitution with the product of oxidation. Now the yield of mellitic acid *does* vary with the sources of the charcoal employed, and the temperature, pressure and duration of carbonization; but the formation of the mellitic acid cannot be attributed to the presence of complex hydrocarbons, possibly retained by the charcoal carbonized at a comparatively low temperature, since a quantitative determination of the percentage of hydrogen, oxygen and nitrogen, invariably accompanying this kind of charcoal, gives not more than 1% of these elements, while the yield of mellitic acid reaches as high a value as 40%. The dark residue "mellogen,"<sup>36</sup> remaining after the first oxidation, gives on exhaustive oxidation again mellitic acid and also some oxalic acid. To attribute the varying yields of mellitic acid to the existence of several modifications of amorphous carbon, as some investigators are inclined to do, is quite unwarranted, as such an explanation of the somewhat varying quality and properties of charcoal would necessitate the assumption of a whole series of modifications of amorphous carbon, corresponding to every source of charcoal and practically to every change of 20° to 50° in the temperature of carbonization. The causes of the dissimilar behavior of various samples of charcoal are probably much simpler. Such causes may be (a) a high temperature of carbonization, which reducing the porosity of the resulting amorphous carbon or charcoal, increases in consequence its resistance to oxidation; (b) a high temperature of carbonization, which facilitates the conversion of amorphous carbon into graphite, so that we may deal with charcoal containing a high percentage of finely divided graphite;<sup>37</sup> (c) a high percentage of mineral matter,

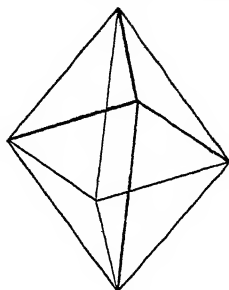


Fig. 6.

<sup>35</sup> Meyer and Steiner, *Monatsh.*, **35**, 475 (1914).

<sup>36</sup> Bartoli and Papasogli, Reference 34.

Dickson and Easterfield, *Proc. Chem. Soc.*, **1898**, 163.

<sup>37</sup> Arsem, *Trans. Am. Electrochem. Soc.*, **20**, 105 (1911).

contaminating charcoal, may affect its properties in more than one way.

Thus we find that there are three distinct forms of carbon, corresponding to the three, theoretically possible, fundamentally different configurations. The following considerations may help to assign to each modification its constitutional formula. The calorimetric measurements of the heat of complete combustion of carbon per gram-atom give<sup>38</sup> for amorphous carbon, 97.650 Cals.; for graphite, 94.810 Cals.; and for diamond, 94.310 Cals. These figures indicate the sum total of the energy liberated during the formation and degradation of the possible complexes<sup>24</sup> plus that of the oxidation of the carbon monoxide to carbon dioxide.

It must be noted that the calorimetric measurements of the heats of combustion of the modifications of carbon differ considerably with every experimenter.<sup>39</sup> Taking equal weights of amorphous carbon, graphite and diamond, and subjecting them to complete combustion, we find that the amount of heat evolved is different for each form of carbon, although the number of atoms taken and the number of molecules of carbon dioxide formed is identical in all cases.

Looking for the cause of this dissimilarity of thermic values we are driven to attribute it to the different stabilities of the molecules in the three cases, which must depend upon the mode of linkage of the units constituting the molecule, as well as the complexity of the molecule itself.

Returning to our classification of theoretically possible configurations we expect that the least stability will be exhibited by molecules whose units have the power of free rotation or, in other words, which have more than one free valence; the maximum stability will be found in the molecule, all constituent units of which are in a state of rigidity and all valences fixed; the intermediate case being a molecule which has some valences free, but a rigid structure.

Now considering the fact that the greater the stability the smaller will be the evolution of heat on complete combustion (compare the case of phosphorus), and correlating this with the calorimetric measurements quoted above, we find that amorphous carbon is represented by Class I, where *none of the atoms* is rigid; graphite by Class II, where the atoms are rigid, but *some* valences free; and diamond by Class III, in which all atoms are rigid and *all* valences fixed. These deductions find strong support in the character of the products of the moist oxidation of carbon. The molecule of amorphous carbon with none of its units rigidly fixed, as might be expected, is the least resisting to oxidants and yields mellitic

<sup>38</sup> Berthelot and Petit, *Ann. chim.*, [VI] 18, 89, 98 (1889).

<sup>39</sup> Favre and Silberman, *ibid.*, [III] 35, 357 (1852).

Mixter, *Am. J. Sci.*, [IV] 19, 440 (1905).

Roth and Wallasch, *Ber.*, 46, 896 (1913).



acid. Graphite with its partly fixed units gives rise to graphitic oxide or acid, an acid more complex than mellitic. The rigidly fixed units of diamond are practically unaffected under the same conditions of oxidation.<sup>35,40</sup>

Similar to the heats of combustion we may expect the values of any other physical property to show a regular gradation from amorphous carbon to the diamond, the value for graphite lying between the values for the two other forms, such gradation serving as confirming evidence in support of the theory under discussion. Below are collected the values for a number of physical constants, which have been determined for all three forms of carbon. The numbers are taken from Landolt-Börnstein, "Tabellen," 4th Edition, 1912.

TABLE I.  
Properties of Carbon.

	Density.	Coefficient of cubical expansion.	Thermal conductivity.	Specific heat. <sup>42</sup>	Electrical conductivity.
Diamond	3.51	0.00000375	0.33(0°) <sup>41</sup>	0.1128(10.7°)	$\left\{ \begin{array}{l} 0.211 \times 10^{-14} \text{ to} \\ 0.309 \times 10^{-13} (15^\circ) \end{array} \right.$
Graphite	2.10-2.32	0.0000104	0.0117	0.1604 <sup>a</sup> (10.8°)	0.0802 $\times 10^4$ (15°)
Amorphous carbon					
Gas coke	1.885	0.0000162			
Coconut charcoal	1.67-1.86				
Lamp black, sugar charcoal and wood charcoal	1.70-1.80		0.000405	0.1653(0-24°)	0.25(12°)

<sup>a</sup> Ceylon graphite.

An inspection of this table shows that, with the single exception of the electrical conductivity, all the physical properties are in the order we should expect. In the case of the electrical conductivity graphite occupies an anomalous position, in that its conductivity is very much greater than that of either the diamond or amorphous carbon. The explanation may be found in the fact that in diamond *all* electrons, being immobilized in linkages, leave *none* free to conduct a current, while in graphite the single free valence, serving as a directive, polar force, facilitates the electric current. Amorphous carbon with its several free valences—counter-acting forces—occupies an intermediate position.

The elucidation of the molecular structure of the carbon allotropes throws much light upon the mechanism of the combustion of carbon, a problem which has received a good deal of attention.

<sup>40</sup> Meyer, *Ber.*, **4**, 801 (1871); *Ann.*, **180**, 175 (1875).

Schulze, *Ber.*, **4**, 802, 806 (1871).

Standenmaier, *ibid.*, **31**, 1481 (1898); **32**, 1394, 2824 (1899).

Dickson and Easterfield, Reference 36.

<sup>41</sup> Eucken, *Physik. Z.*, **12**, 1005 (1911).

<sup>42</sup> Weber, *Pogg. Ann.*, **154**, 367, 553 (1875).

Under the stress of experimental evidence the *reduction theory* of Lang<sup>43</sup> has been replaced by that of *gradual oxidation* by Baker<sup>44</sup> and Dixon,<sup>45</sup> which in its turn is being replaced by the *theory of complexes*, proposed by Rhead and Wheeler.<sup>24</sup>

The conception of a non-rigid configuration containing free valences, for amorphous carbon, affords a complete explanation of (1) the comparatively easy combustibility of this form of carbon; and (2) the simultaneous evolution of carbon monoxide and dioxide, products of disruption of the complexes, logically constituting the first stage of oxidation. The conception of a rigid configuration for diamond and graphite explains the considerable resistance to combustion exhibited by these allotropes, and suggests that no intermediate complexes, assumed in the case of amorphous carbon, are likely in the course of combustion of diamond.

### Allotropy of Iron and Nickel.

The lack of distinctive chemical properties makes the recognition of separate forms of iron practically dependent upon the variation of physical properties, as indicated by transition points. The study of the graphs, representing the changes of temperature, volume,<sup>46</sup> tenacity, electrical conductivity<sup>47</sup> and the solubility of carbon and hydrogen<sup>48</sup> indicates there transition points, *viz.*, at 769°, 906° and 1401°, the solidification point<sup>49</sup> of iron lying at 1528°.

The precision of the determinations of the transition points is greatly influenced by the impurities (carbon, hydrogen, nickel, etc.) persistently

<sup>43</sup> Lang, *Z. physik. Chem.*, **2**, 62 (1888).

<sup>44</sup> Baker, *Phil. Trans.*, [A] **179**, 571 (1888).

<sup>45</sup> Dixon, *J. Chem. Soc.*, **69**, 774 (1896); **75**, 630 (1899). See also Johnson and McIntosh, *Trans. Roy. Soc. Canada*, [III] **7**, 161 (1913); Müller, *Z. angew. Chem.*, **33**, 36 (1920).

<sup>46</sup> Gore, *Proc. Roy. Soc.*, **17**, 260 (1869).

Barrett, *Phil. Mag.*, [4] **46**, 472 (1873).

Osmond, *J. Iron Steel Inst.*, **49**, 180 (1896).

Pionchon, *Compt. rend.*, **102**, 1145 (1886).

Osmond, *ibid.*, **103**, 743 (1886).

Heyn, *Stahl u. Eisen*, **20**, 625 (1900).

Rooseboom, *Z. physik. Chem.*, **34**, 437 (1900).

Tammann, *Z. anorg. Chem.*, **37**, 448 (1903).

Charpy and Grenet, *Compt. rend.*, **139**, 567 (1904).

Burgess and Crowe, *J. Washington Acad. Sci.*, **3**, 329 (1913).

Broniewski, *Compt. rend.*, **156**, 669 (1913).

Ruer and Klesper, *Ferrum*, **11**, 257 (1914).

<sup>47</sup> Le Chatelier, *Z. physik. Chem.*, **8**, 183 (1891).

Fournel, *Compt. rend.*, **143**, 46 (1906).

<sup>48</sup> Benedicks, *Z. physik. Chem.*, **40**, 545 (1902).

Sieverts, *ibid.*, **77**, 591 (1911).

Jurisch, *Stahl u. Eisen*, **34**, 252 (1914).

<sup>49</sup> Ruer and Goerrens, *Ferrum*, **13**, 1 (1915).

accompanying iron. The presence of these impurities results in the depression of the transition points, which converge gradually to one point at  $700^{\circ}$ .<sup>50</sup> The persistence of impurities in iron can be seen from the fact that electric measurements of even the purest iron show as much as 0.27% of carbon<sup>48</sup> (0.08% according to Fournel<sup>47</sup>).

The experimental data on the comparative hardness of the modifications of iron are conflicting, owing to the disturbing factors of the different solubilities and varying percentages of dissolved carbon,<sup>51</sup> etc. While the  $\beta \rightleftharpoons \gamma$  and the  $\gamma \rightleftharpoons \delta$  transitions, as indicated by the specific heat, thermal measurements,<sup>52</sup> electrical resistance, change of crystal structure,<sup>53</sup> dilation,<sup>54</sup> electromotive forces<sup>55</sup> and magnetism,<sup>56</sup> are definite and sudden, the  $\alpha \rightleftharpoons \beta$  transition is gradual, extending over a range of  $40^{\circ}$  to  $100^{\circ}$ , and is accompanied by a change of magnetic properties.<sup>57</sup> The study of the specific heat indicates that the  $\alpha \rightleftharpoons \beta$  transformation is completed by a continuous series of mixed crystals.<sup>58</sup> These fundamental differences revealed in the course of a comparative study of the transition points of iron make it manifest that the  $\alpha \rightleftharpoons \beta$  critical point, or rather range, cannot be regarded as a true allotropic change.<sup>52,59</sup> The  $\alpha \rightleftharpoons \beta$  transformation point may be regarded as merely the termination of the  $\alpha \rightleftharpoons \gamma$  change. The  $\beta$  form is simply a solid solution of  $\gamma$  in  $\alpha$ , the proportion of  $\gamma$  iron increasing with temperature.<sup>60</sup> Thus  $\alpha \rightleftharpoons \beta$  is the point at which  $\gamma$  ceases to be metastable and becomes unstable. This point is enhanced by impurities becoming in quenched steel as definite as the  $\beta \rightleftharpoons \gamma$  point,<sup>58</sup> and vanishes gradually with the decrease of the percentage of solid and gaseous matter dissolved in the iron.<sup>61</sup>

<sup>50</sup> Osmond, *Compt. rend.*, **103**, 1135 (1886).

Rooseboom, Reference 46.

<sup>51</sup> Benedicks, Reference 48.

Skrabal, *Z. Elektrochem.*, **10**, 749 (1904).

Rosenhain and Humphrey, *Proc. Roy. Soc.*, **83A**, 200 (1910).

<sup>52</sup> Honda, *Science Repts. Tohoku Imp. Univ.*, [1] **2**, 69 (1913).

Carpenter, *J. Iron Steel Inst.*, **87**, 315 (1913).

<sup>53</sup> Burgess and Kellberg, *J. Washington Acad. Sci.*, **4**, 436 (1914).

<sup>54</sup> Rosenhain and Humphrey, *J. Iron Steel Inst.*, **87**, 219 (1913).

Benedicks, *ibid.*, **89** 440 (1914).

Driesen, *Ferrum*, **13**, 27 (1915).

<sup>55</sup> Benedicks, *Compt. rend.*, **162**, 297 (1916).

<sup>56</sup> Ishiwara, *J. Iron Steel Inst.*, **97**, 551 (1918).

<sup>57</sup> Osmond, *Ann. Mines*, **17**, 110 (1900).

Osmond and Cartand, *ibid.*, **18**, 113 (1900).

Boudouard, *J. Iron Steel Inst.*, **63**, 299 (1903).

<sup>58</sup> Oberhoffer, *Stahl u. Eisen*, **27**, 1764 (1907).

Carpenter and Stead, *J. Iron Steel Inst.*, **88**, 119 (1913).

<sup>59</sup> Honda, *Science Repts. Tohoku Imp. Univ.*, **6**, 217 (1917).

<sup>60</sup> Benedicks, *J. Iron Steel Inst.*, **86**, 242 (1912).

<sup>61</sup> Carpenter, *ibid.*, **87**, 326 (1913).

The loss of magnetism at the  $\alpha \rightleftharpoons \beta$  point is therefore due not merely to the increased velocity of vibration of the molecules, but to the formation of  $\gamma$  in  $\alpha$  iron, the former not only reducing the "effective section" of the conducting substance, but also breaking the current lines, when beyond a certain limit, thus resulting in a rapid fall of intensity in the magnetic forces.<sup>62</sup> Another view is that the  $\alpha \rightleftharpoons \beta$  transformation, accompanied by loss of magnetism, is a polymorphic change, magnetism being due either to a polar arrangement of molecules,<sup>63</sup> or to a specific property of the  $\alpha$  form of iron.<sup>64</sup>

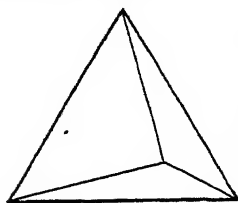
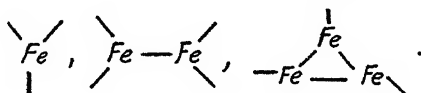


Fig. 7.

Thus we find that the  $\alpha$ ,  $\gamma$  and  $\delta$  iron are the forms recognized as having a separate existence.<sup>65</sup>

Now in the light of the theory of allotropy, a trivalent element (as iron always is potentially) may exist in two distinct molecular forms: (I) a saturated molecular configuration, having no free valences (see Fig. 7), and (II) an unsaturated molecular form, having free valences;



Considering that practically all experimental evidence tends to show that the  $\alpha \rightleftharpoons \beta$  point is merely a retardation of the  $\alpha \rightleftharpoons \gamma$  transition point, thus disposing of the  $\beta$  form, and also the fact that the  $\gamma \rightleftharpoons \delta$  point, although sharply defined, is of a considerably smaller magnitude than the  $\alpha \rightleftharpoons \gamma$  change, we may take the two theoretically possible forms to correspond to the  $\alpha$  and  $\gamma$  forms of iron.

Considering that (a) generally molecular complexity decreases with the rise of temperature, and that (b) according to the magneton theory<sup>66</sup> molecular complexity decreases from  $\alpha$  to  $\gamma$ , we may take it that the  $\alpha$  form is represented by the saturated molecular configuration (tetrahedron), and  $\gamma$  by an unsaturated molecular form. The  $\delta$  modification formed at high temperature and differing from  $\gamma$  to a less degree than  $\alpha$ , can be re-

<sup>62</sup> Benedicks, *J. Iron Steel Inst.*, **87**, 333 (1913); also **89**, 440 (1914).

Honda, *ibid.*, **99**, 457 (1919).

Oknov, *Ferrum*, **11**, 1 (1913).

Driesen, *ibid.*, **13**, 27 (1915).

Lashchenko, *J. Russ. Phys. Chem. Soc.*, **46**, 311 (1914).

<sup>63</sup> Le Chatelier, *Compt. rend.*, **136**, 664 (1903).

Hilpert, *Z. Elektrochem.*, **16**, 390 (1910).

<sup>64</sup> Weiss, *Rev. metal.*, **6**, 680 (1908).

Sauveur, *J. Inst. Metals*, **88**, 171 (1913).

<sup>65</sup> Honda, *J. Iron Steel Inst.*, **91**, 199 (1915).

<sup>66</sup> Weiss, *Compt. rend.*, **152**, 688 (1911).

garded<sup>67</sup> as an *allotropoid*; *i. e.*,  $\gamma$  and  $\delta$  both belong to the same type or class of molecular configuration (unsaturated), but each differs from the other in complexity,  $\gamma$ -iron being represented by a tri-atomic and  $\delta$  iron by a di-atomic molecule.

The vapor of iron is probably mono-atomic, similar to mercury, phosphorus and the halogens at high temperature. The vapor of iron would thus together with  $\gamma$  and  $\delta$  iron form three allotropoids, belonging to the same type of molecular configuration. The molecular complexity of the modifications of iron may thus be represented in the following tabular form.

Forms of iron.	Transition temperatures. ° C.	Minimum molecular complexity, or number of atoms in the molecule.
$\alpha$	906	4
$\gamma$	1401	3
$\delta$	1528	2
Vapor		1

The conception of the various forms of iron as being due not to molecular differences, but to different groupings of atoms<sup>68</sup> explains nothing, and represents a misinterpretation of the recent X-ray spectrometric work.

### Allotropy of Nickel.

The transformation of nickel has received considerably less attention than that of iron. Nevertheless sufficient data are available to show that the main transition point lies at 345–346°, being accompanied by a change in the rate of loss of permeability, coefficient of expansion, specific heat, magnetic and thermo-electric properties and electrical conductivity.

The fact that the several determinations of the transition point of nickel vary within 20° to 25°, is probably due not only to the different methods of determination, but also in a large degree to the different states of purity of the nickel under investigation.

A second transition point, decidedly less pronounced, accompanied by a change in crystalline form, has been observed<sup>69</sup> at 700°. These transition-points resemble the  $\beta \rightleftharpoons \gamma$  and  $\gamma \rightleftharpoons \delta$  changes in iron, and we can with sufficient justification draw the same conclusion as to the molecular complexity of the forms of nickel, as in the case of iron.

<sup>67</sup> Desch, *Trans. Faraday Soc.*, **11**, 136 (1916).

<sup>68</sup> Oxley, *ibid.*, **11**, 129 (1916).

<sup>69</sup> Tomlinson, *Phil. Mag.*, [5] **25**, 372 (1888).

Harrison, *ibid.*, [6] **7**, 626 (1904).

Schlott, *Ann. Physik.*, [4] **26**, 201 (1908).

Schukoff, *J. Russ. Phys. Chem. Soc.*, **40**, 1784 (1908).

Werner, *Z. anorg. Chem.*, **83**, 275 (1913).

Cohen, *Z. Elektrochem.*, **15**, 686 (1909).

Lashchenko, Reference 62.

Jänecke, *Z. angew. Chem.*, **31**, 229 (1918).

In conclusion the author wishes to thank Messrs. W. Lamb and G. Greenwood for revising the literature on phosphorus and iron respectively.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

# AROMATIC MERCURI-ORGANIC DERIVATIVES. THE HOFMANN REARRANGEMENT AND THE NATURE OF VALENCES OF MERCURY IN MERCURI-ORGANIC DERIVATIVES.

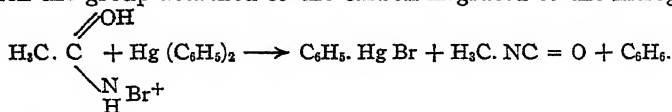
BY MORRIS S. KHARASCH.<sup>1</sup>

Received January 29, 1921.

The effect of the halogens on mercury diphenyl has been studied by Otto<sup>2</sup> who found that bromine (one molecule) in water solution or in anhydrous media, gave rise to phenyl mercury bromide, and phenyl bromide. When, however, an excess of bromine was used, the resulting products were mercuric bromide and phenyl bromide. The behavior of mercury diphenyl with bromine is representative of the behavior with any other halogen. With the halogen acids the result was similar but, of course, instead of the phenyl halide, benzene was the other product. It was, therefore, of interest to find out just what the effect of positive halogen<sup>3</sup> alone on mercury diphenyl would be.

It was with this idea in mind that the effect of N-bromo-acetamide in sodium-dried benzene upon mercury diphenyl, dissolved in the same solvent, was tried. After the solution was warmed for about 10 minutes on the water-bath, a solid separated which was identified as phenyl mercury bromide.<sup>4</sup>

The reaction when studied in greater detail, and also, with other N-bromo-amides revealed the fact that mercury diphenyl played the same part in this reaction as sodium hydroxide in aqueous solution and sodium ethylate in absolute alcohol,<sup>5</sup> and that it also led to a rearrangement in which the group attached to the carbon migrated to the nitrogen.



<sup>1</sup> National Research Fellow in Organic Chemistry.

<sup>2</sup> Otto, *J. prakt. Chem.*, [2] 1, 182 (1870).

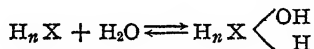
<sup>3</sup> Seliwanow, *Ber.*, 25, 3617 (1892); Lengfeld and Stieglitz, *Am. Chem. J.*, 15, 215, 504 (1893); W. A. Noyes, *THIS JOURNAL*, 23, 450 (1901); J. Stieglitz, *ibid.*, 23, 796 (1901), etc.

<sup>4</sup> The same reaction takes place also in bright sunlight in the course of a few minutes, without any heating whatsoever.

<sup>5</sup> Lengfeld and Stieglitz, *Am. Chem. J.*, 15, 215, 504 (1893).

Furthermore, we find that just as sodium hydroxide or sodium ethylate fails to effect a rearrangement in the case of the N-substituted alkyl or aryl bromo- and chloro-acetamides,<sup>6</sup> so mercury diphenyl seems not to be acted upon by the latter reagent. Even after prolonged boiling (12 to 14 hours), no action occurs, although N-chloro-acetanilide is a chlorinating agent in anhydrous media. Thus, when the latter was treated with aniline in dry benzene, 2,4-dichloro-aniline and acetanilide were formed. Also dimethyl aniline, diphenylamine, and *m*-dimethylamino-acetyl phenol gave acetanilide and chlorinated products, while triphenylamine and *m*-nitro-dimethylaniline were not acted upon at all.

Thus, the reaction of mercury diphenyl and the N-bromo amides affords an excellent illustration of the basicity of mercury diaryl compounds. Of course, we must distinguish bases derived from hydrides which acquire their basicity through two additional valences, one positive and one negative, forming



where X is negative, such as ammonium, sulfonium, oxonium, iodonium and similar bases, and those derived from metal hydroxides, M(OH)<sub>2</sub>, where M is positive, *e. g.*, the derivatives of zinc, magnesium, mercury, etc. Mercury compounds of the type R-Hg-R and R-Hg-OH could well be, and probably are, derived from mercuric hydroxide Hg(OH)<sub>2</sub> giving

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them the structure R-Hg-R and R-Hg-OH respectively. In the case of the latter compounds, which are strong bases, the substitution could easily bring out the high ionizing tendency of a univalent base, comparable with silver hydroxide. Mercury diaryl compounds in benzene solution are then quite comparable to calcium hydroxide in aqueous solution,<sup>7</sup> which may be considered as the metal hydroxide or salt of the very weak

++ —  
acid water. Mercury diphenyl Hg (R)<sub>2</sub> is therefore a base of the benzene  
+ —  
system, as sodium amide NaNH<sub>2</sub> is a base of the ammonium system, sodium hydroxide of the aqueous system, etc.

A different view point as to the electronic structure of mercury dialkyl and diaryl compounds is held by Jones and Werner.<sup>8</sup> These authors assume that in these substances one of the valences of mercury functions positively and the other negatively, *i. e.*, to give a compound of the type

<sup>6</sup> Stieglitz and Slosson, *Ber.*, 28, 3266; 34, 1613 (1901); Slosson, *Am. Chem. J.*, 29, 289 (1903).

<sup>7</sup> The same view point has been maintained by Stieglitz for some years for the zinc methyl derivatives. Stieglitz, "Qualitative Chemical Analyses," 1, 177 (1911). See also Jones, *THIS JOURNAL*, 40, 1250 (1918).

<sup>8</sup> Jones and Werner, *ibid.*, 40, 1257 (1918).

— + — +

R-Hg-R. The experimental evidence for this assumption is confined to the study of the behavior of mercury diethyl, di-*iso*-amyl and dibenzyl. At high temperatures, these decompose to give metallic mercury and a

+ —

hydrocarbon R-R. Upon hydrolysis with glacial acetic acid, again at high temperatures, these give, for instance, in the case of mercury dibenzyl, metallic mercury, benzyl acetate, toluene and dibenzyl.

Jones and Werner, therefore, infer that if a compound upon hydrolysis gives metallic mercury, an alcohol, and a hydrocarbon, its electronic struc-

— + — +

ture must be R-Hg-R. While the validity of such reasoning is unquestioned it can be shown very readily that Jones and Werner's experimental data do not necessitate such a conclusion—one that is quite in disagreement with the position of mercury in the periodic system—and that direct experimental evidence that the valences of mercury function in any way but positively in all mercuri-organic derivatives is still lacking.

In the first place, we know that mercury in all inorganic compounds functions positively, and we should expect, therefore, that a bond between negatively charged mercury and a positive radical would be less stable than one between a positive mercury and a negative radical. This is in direct contradiction to Jones and Werner's formula which requires that the more stable union be ruptured first, when compounds of the type

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R-Hg-R are treated with acids, the following taking place, according to Jones and Werner.

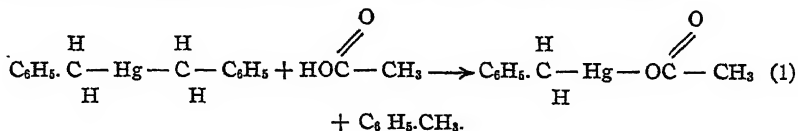


Furthermore, Jones and Werner seem to ignore entirely the fact that mercuric ion is an oxidizing agent, the oxidizing power of which increases with the temperature. Thus stannous ion is oxidized by mercuric ion to the stannic ion, even at ordinary temperatures. Again, a good many organic compounds more or less sensitive to oxidation are oxidized by mercuric ion; dimethyl-*p*-phenylene-diamine is first oxidized to Wurster's red by a solution of mercuric acetate, and at a somewhat higher temperature metallic mercury is thrown out. The same is true of hydroquinone. In view of these facts one must always be on the lookout for the oxidizing tendency of the mercuric ion especially when working with mercury compounds at high temperatures.

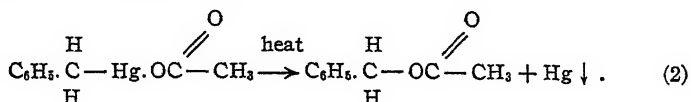
If we bear this fundamental property of mercury in mind, the reactions of aryl and alkyl mercury compounds studied by Jones and Werner do not then necessitate the assumptions made by those writers. Thus, they started with 15 g. of mercury dibenzyl and after heating it for 7 hours at 200° isolated the following products in the quantities given: mercury 7.776 g.; toluene, 1.756 g.; benzyl acetate, 2.267 g.; dibenzyl,



3.05 g. These results show convincingly that two reactions took place simultaneously. In the first place, part of the mercury dibenzyl, namely 7.9 g., was transformed into metallic mercury and dibenzyl,<sup>9</sup> and the rest (7.1 g.) into mercury, toluene and benzyl acetate. In the latter case, the reaction undoubtedly takes place in the following stages.



In the benzyl mercuric acetate thus formed, at the high temperature used, the doubly positive mercury atom oxidizes the carbon and we get benzyl acetate and mercury, *i. e.*,



There is, therefore, nothing unusual about all the reactions mentioned by Jones and Werner. The reaction is simply a case of intramolecular oxidation and reduction and quite comparable with the molecular rearrangements which take place due to intramolecular oxidation and reduction.<sup>10</sup> Again, the decomposition of mercury compounds by chlorine, bromine and iodine, taken in connection with the decomposition by acids,<sup>11</sup> lends more weight to the well accepted fact that mercury always functions positively in all mercuri-organic compounds.

We might add also that at no time do results obtained by the use of high temperatures prove anything as to the electronic structure of the starting product. As yet, we are quite ignorant of the changes which take place at high temperatures. Thus, the formation of diphenyl alone, at a high temperature, from benzene would be a very poor argument that, in benzene, we have two tautomeric electromers in equilibrium:  $\text{C}_6\text{H}_5\text{--H} \rightleftharpoons \text{C}_6\text{H}_5\text{--H}$ ; and Jones and Werner carried out the hydrolysis of mercury dialkyl and diaryl compounds at temperatures ranging from 170° to 220°.

<sup>9</sup> This observation was made by Wolff [*Ber.*, 46, 64 (1913)] who states that when mercury dibenzyl is heated above its melting point, 111°, it is decomposed into metallic mercury and dibenzyl.

<sup>10</sup> L. W. Jones, *Am. Chem. J.*, 48, 1 (1912); 50, 440 (1913). J. Stieglitz, *Ber.*, 43, 782 (1910); *This Journal*, 36, 287 (1914); *Ber.*, 46, 2149 (1913).

<sup>11</sup> Jones and Werner have to assume the existence of two tautomeric electromers  $\text{R--Hg--R} \rightleftharpoons \text{R--Hg--R}$ , to explain the decomposition of mercury dialkyl and diaryl compounds by conc. hydrochloric acid, *i. e.*, mercuricchloride and a hydrocarbon being the products.

Summing up, we might say that from experimental work described in this paper, and the behavior of mercury diaryl compounds, in general,

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the structure  $R-Hg-R$  is the most appropriate one: it explains the reactions of mercury diaryl and dialkyl compounds without any additional postulates and is in perfect agreement with the chemistry of the element.

### Experimental.

**Action of Mercury Diphenyl on N-Bromo-amides. N-Bromo-acetamide.**—Of this 0.6 g. was dissolved in dried benzene,<sup>12</sup> and then treated with 1.3 g. of mercury diphenyl dissolved in 40 cc. of benzene. The solution was then boiled for 20 minutes at the end of which time no active bromine could be detected in it. A white crystalline compound separated, and the solution had a pungent, irritating odor very characteristic of an isocyanate. The precipitate was collected on a filter, care being taken not to allow any atmospheric moisture to come in contact with the filtrate. The precipitate thus obtained (0.7 g.) melted at 276°. After a single crystallization it melted at 291°. When the compound was mixed with some known phenyl mercuric bromide the melting point of the latter was not lowered.

The filtrate from the phenyl mercury bromide contained some phenyl mercury bromide, a little unchanged mercury diphenyl and methyl isocyanate. To separate the latter from other compounds, dry aniline was added<sup>13</sup> to the filtrate to form methyl-phenyl urea. The mixture was warmed for 3 minutes at 60°, cooled and ligroin added until the solution became turbid. Beautiful white needles were thus obtained, m. p. 152° to 153°. The melting point of  $\alpha,\beta$ -phenyl-methyl urea given in the literature is 150°.

The urea thus obtained exhibits the reactions given in the literature for phenyl-methyl urea ( $\alpha, \beta$ ), *i. e.*, when a minute quantity of it was dissolved in conc. sulfuric acid and a little powdered potassium dichromate added to it, an intense maroon color was imparted to the solution.

The same arrangement is also effected if the solution of N-bromo-acetamide and mercury diphenyl is allowed to stand in bright sunlight for 3 to 4 minutes. In the dark however, the reaction takes place very slowly as indicated by the fact that after a lapse of two weeks there was still a considerable quantity of unchanged N-bromo-acetamide in the solution.

**N-Bromobenzamide.**—2 g. of this substance was dissolved in 100 cc. of hot benzene and 3.4 g. of mercury diphenyl dropped into the solution. It was then put out in the sunlight. After 20 minutes a considerable quantity of phenyl mercury bromide separated. The reaction, however, did not go to completion, as indicated by the presence of active bromine in the solution. To complete the reaction the solution was boiled on the water-bath for one hour longer. The precipitate (2.5 g.) was collected on a filter paper and identified as phenyl mercury bromide. To the filtrate aniline was added, and after 3 to 4 minutes a precipitate began to separate. It was allowed to stand for 20 minutes and the precipitate (0.8 g.) then collected on a filter paper, m. p. 231°. The melting point of symmetrical diphenyl urea given in the literature is 230°, mixed m. p. 230°.

<sup>12</sup> Throughout this investigation, only sodium-dried benzene was used.

<sup>13</sup> Since only small amounts of material were used throughout this investigation, it was thought advisable to solate the urea derivatives by treating the isocyanates in solution with aniline rather than the free isocyanates.

By working up the filtrate from symmetrical diphenyl urea some more phenyl mercury bromide, a little unchanged mercury diphenyl and also an appreciable quantity of the symmetrical diphenyl urea were obtained.

***m*-Nitro-*N*-Bromobenzamide.**—To 0.7 g. of *m*-nitro-*N*-bromobenzamide dissolved in 180 cc. of benzene 1 g. of mercury diphenyl was added. After 1 hour it still gave a positive test for active bromine, and the reaction was only complete after 2 <sup>3</sup>/<sub>4</sub> hours' boiling. The precipitate (0.4 g.) that separated was identified as phenyl mercury bromide. From the filtrate after the addition of aniline and then ligroin a yellow crystalline compound (0.3 g.) was obtained which was identified as *m*-nitro-carbanilide, m. p. 197°. This melting point is not lowered by mixing the compound with known *m*-nitro-carbanilide.

The filtrate from the urea when evaporated to dryness and then worked up yielded some more phenyl mercury bromide and also *m*-nitro-carbanilide.

*o*- And *p*-nitro-*N*-bromobenzamides were treated in the same way as the *meta* isomer. The time of heating was from 2 to 3 hours. When worked up like the *meta* compound they yielded phenyl mercury bromide and the corresponding nitro-carbanilides which were identified by their melting points.

### Action of *N*-Chloro-acetanilide on Various Compounds.

**Mercury Diphenyl.**—*N*-chloro-acetanilide (0.84 g.) was dissolved in 80 cc. of sodium-dried benzene and then 1.7 g. of mercury diphenyl added to it. The solution was then boiled for 14 hours, but even at the end of that time it still gave a strong test for active chlorine, and the mercury diphenyl was recovered by distilling the benzene *in vacuo*, and extracting the *N*-chloro-acetanilide with ligroin.

**Aniline.**—*N*-chloro-acetanilide (2 g.) was dissolved in 60 cc. of sodium-dried benzene and 0.6 g. of aniline added to it. The resulting solution was perfectly colorless, but turned dark after boiling it for 4 minutes. The reaction was complete in 20 minutes as indicated by the fact that the test for positive chlorine failed. Upon cooling a crystalline compound separated, (0.8 g.), which, after crystallization, melted at 114°. Its melting point was not lowered by mixing it with pure acetanilide.

To the filtrate from the acetanilide was added acetyl chloride to convert the dichloro-aniline into its acetyl derivative, and the mixture was warmed 10 minutes. The benzene solution was washed three times with water to destroy the excess of acetyl chloride, dried with sodium sulfate, and the benzene distilled. Crystals were thus obtained which upon crystallization melted at 146°. The melting point of 2,4-dichloro-aniline given in the literature is 147°; mixed m. p. 147°.

When dimethylaniline was used in place of aniline, acetanilide was also obtained and an oil, which was probably 2,4-dichloro-dimethylaniline. The latter compound is described in the literature as an oil.

### Summary.

1. It has been shown that the Hofmann Rearrangement takes place when various acyl halogen amides, in sodium-dried benzene, are treated with mercury diphenyl.

2. It has been demonstrated that mercury diphenyl acts as a base in benzene solution.

3. A convenient method for the preparation of isocyanates is described.

4. It has been pointed out that the structure,  $\text{R}-\overset{\text{---}}{\text{Hg}}-\overset{\text{---}}{\text{R}}$ , for mercury

diaryl compounds has no sound theoretical or experimental basis, and the structure  $\begin{smallmatrix} - & + & + & - \end{smallmatrix}$  R-Hg-R is supported.

5. It has been shown that N-chloro-acetanilide has no effect on mercury diphenyl, although it is a good chlorinating agent.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE.]

## MERCURI-ORGANIC DERIVATIVES. THE MERCURIZATION OF AROMATIC AMINES AND ITS RELATION TO THE THEORY OF SUBSTITUTION.

BY MORRIS S. KHARASCH<sup>1</sup> AND ISADORE M. JACOBSON.<sup>2</sup>

Received February 15, 1921.

The principles underlying the mercurization of aromatic compounds have occupied the attention of one of us (Kh.) for the past two years. The important fact that, in a mono-substituted benzene derivative, the mercury enters *para* or *ortho* to the group already present in the molecule, was pointed out early by Dimroth,<sup>3</sup> and has been substantiated by the vast amount of experimental work done by others. This fact of *ortho* and *para* substitution is particularly striking when one attempts to apply the theories of substitution to mercurization since mercury never enters *meta* to the group already present in the molecule. Even where the usual rules of substitution require that a *meta* derivative be formed, *e. g.*, with benzoic acid, benzophenone, and nitrobenzene, only *ortho* substituted mercury compounds have been isolated.

The phenomenon of mercurization was considered by Dimroth to be similar to that of nitration, sulfonation, etc., in the sense that the position taken by the entering mercury in compounds containing groups now considered electro-negative, *e. g.*, amino or hydroxyl groups, was quite in agreement with the rule of Crum Brown and Gibson. He considered the exceptional behavior of nitrobenzene, benzoic acid, and benzophenone as anomalous reactions which needed to be accounted for. However, until recently, no effort has been made to explain the orientation of mercury in the benzene molecule.<sup>4</sup> The rule of Crum Brown and Gibson, being purely empirical, offers no suggestion as to the mechanism of the

<sup>1</sup> National Research Fellow in Organic Chemistry.

<sup>2</sup> The material presented here is used by I. Jacobson in his dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

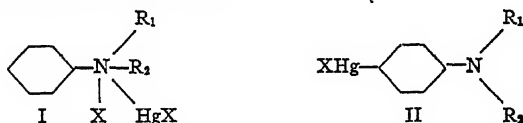
<sup>3</sup> Dimroth, *Ber.*, **35**, 2853 (1902).

<sup>4</sup> Schoeller, Schrauth, and Liese (*Ber.*, **52B**, 1777 (1919)) apply the theory of Armstrong for substitution in aromatic amines to mercurization, the limitations of which theory will be pointed out later.

reaction, nor does it help to predict whether a compound could be mercurized or not. Therefore, it appeared desirable to apply some of the modern theories of substitution to the orientation of mercury in the benzene molecule.

In the present paper, the authors will confine themselves to the mechanism of mercurization of aromatic amines and also attempt to show that the mechanism suggested for mercurization may be extended to explain satisfactorily orientation of other groups in the case of aromatic amines. It will be shown further, in a condensed critical survey of the theories of others, that none of these is completely satisfactory. For example, most of them fail to account for the fact that dimethylaniline is mercurized readily.

The theory which the present authors have been led to adopt as a result of their extended experimental work, briefly stated, is as follows. The mercurization of an aromatic amine proceeds in two stages: first, the formation of an ammonium salt with the mercuric acetate or chloride to give a compound of the general type I.



This compound is then rearranged to the more stable configuration having the mercury radical attached to carbon, (Type II), the *para* position being usually favored.<sup>5</sup> If this position is already occupied, the mercury goes to the *ortho* position. Furthermore, it is only the ammonium salt that undergoes rearrangement,<sup>6</sup> the instability of the salt being due to the presence of an electropositive group or atom on the amino nitrogen.<sup>7</sup>

This, it will be noted, is the application to mercurization of the theories of substitution of Armstrong,<sup>8</sup> Bamberger,<sup>9</sup> Chattaway<sup>10</sup> and others, and

<sup>5</sup> The fact of rearrangement may be due to a smaller energy content on the part of the rearranged compound. This relationship was shown to hold by Rother and Stoermer (*Ber.*, 46, 260 (1913)) for a number of compounds, *e. g.*, cinnamic acid and the isomeric allocinnamic acid.

<sup>6</sup> Acree and Johnson, *Am. Chem. J.*, 38, 265 (1905), have demonstrated that, in the rearrangement of N-chloro-acetanilide, it is the salt and not the free base that rearranges. They fail, however, to attach any importance to the positive charge on the rearranging group, a fact which has already been pointed out by Stieglitz and Stagner, *This Journal*, 38, 2057 (1916).

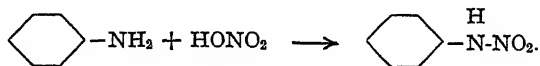
<sup>7</sup> Acree and Johnson, *Am. Chem. J.*, 38, 265 (1905), have shown that, when N-chloro-acetanilide is treated with hydrogen bromide, the speed of the rearrangement is a thousand times greater than when hydrogen chloride is used, and that the end product of the rearrangement is *p*-bromo-acetanilide, instead of *p*-chloro-acetanilide.

<sup>8</sup> Armstrong, *J. Chem. Soc.*, 51, 258, 583 (1887).

<sup>9</sup> Bamberger, *Ber.*, 27, 586 (1894).

<sup>10</sup> Chattaway, *J. Chem. Soc.*, 75, 1048 (1899).

of the general theory of catalysis advanced by Stieglitz,<sup>11</sup> Acree<sup>12</sup> and others that acid catalysts act through salt formation.<sup>13</sup> However, the theory advanced by the present authors diverges from that of Armstrong, Bamberger, and Chattaway, and also from recent theory of mercurization of Schoeller, Schrauth and Liese<sup>4</sup> in a few very important aspects. The theories advanced by the above mentioned authors assume that the entrance of a group into the nucleus of an aromatic amine is always preceded by substitution on the amino nitrogen, thus,



However, as an explanation, this is not adequate to account for the mechanism of substitution of tertiary amines, of the type of dimethyl aniline which contains no replaceable hydrogen. Furthermore, they do not emphasize the nature and importance of the catalysts used in substitution, *i. e.*, strong acids. That the rôle played by acid catalysts is that of salt formation has been pointed out very clearly by Stieglitz<sup>11</sup> in his work on the catalysis of imido-esters, as well as by Acree.<sup>12</sup>

We find thus, that the previous hypotheses have to be modified, if they are to explain consistently all the facts of substitution without further assumptions. The hypothesis advanced by the writers to explain the mercurization of aromatic amines lends itself admirably to this purpose. We shall now proceed to illustrate as briefly as possible the basis for this hypothesis and then show that it is quite compatible with the *ortho* and *para* orientation of other groups in the case of aromatic amines.

That mercury has a great affinity for amino nitrogen and for carbon is best illustrated by the readiness with which the mercury-ammonium complexes are formed, and by the great stability of mercury-carbon compounds.<sup>14</sup> It is the combination of this property of mercury to form stable nitrogen and carbon compounds, and the relatively greater stability of the latter, which enables us to attach mercury to the carbon of the benzene ring in the case of aromatic amines.

Within the scope of a series of investigations being carried out by the one of us, work was undertaken upon the mercurization of the N-alkylated

<sup>11</sup> Stieglitz, *Proc. Congress of Arts and Sci.* (St. Louis), IV, 278(1904); *Am. Chem. J.*, **39**, 29 (1908).

<sup>12</sup> Acree, *ibid.*, **37**, 410 (1907).

<sup>13</sup> In this connection, the work of Reilly and Hickinbotham (*J. Chem. Soc.*, **117**, 103 (1919)) on the rearrangement of *n*-butylaniline is quite significant. They found that only those salts which are capable of combining with the amino group effected the rearrangement.

<sup>14</sup> The stability of the mercury-carbon union is a relative term. It depends to a large extent upon the position of the mercury in the molecule and upon the nature of the neighboring groups. This will be discussed in a later paper. See also Stieglitz, Kharasch, and Hanke, *THIS JOURNAL*, **43**, 1186 (1921).

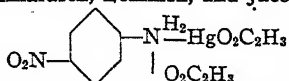
nitro-anilines. It was found that mercurization does not take place when *p*-nitro-dimethylaniline is treated with mercuric acetate in alcoholic solution. Though various experimental conditions were tried, the efforts were futile. It seemed, however, in view of the results of an investigation carried out with other nitro-anilines,<sup>15</sup> that mercurization should take place unless there was some property of the mercurizable nitro-anilines which was not shared by the *p*-nitro-dimethylaniline. Reference to the literature at once revealed the fact that *p*-nitro-dimethylaniline is an extraordinarily weak base. It is precipitated from even conc. hydrochloric acid solution as the free base instead of its hydrochloride, and it does not combine with chloroplatinic acid.<sup>16</sup> Further reference to the literature showed that its *ortho* and *meta* isomers form salts more readily. An investigation of the reactions of these isomers with mercuric acetate showed not only that the reactions are completed within a very short time but at a comparatively low temperature. An attempt was then made to mercurize *p*-nitro-diethylaniline. This met with the same failure as that of the corresponding dimethyl derivative. That this failure to mercurize is not due simply to the fact that the *para* position is occupied was then demonstrated by the fact that *p*-nitro-monomethyl- and *p*-nitro-mono-ethylanilines are mercurized without difficulty, the mercury being oriented to the position *ortho* to the amino group.

These facts, taken in conjunction with the intermediates already isolated<sup>17</sup> and those obtained by Schoeller, Schrauth and Liese,<sup>4</sup> the complex salts of aromatic amines isolated by Klein<sup>18</sup> and the known general fact of the great affinity of mercury for an amino nitrogen, led us to adopt the hypothesis that mercurization proceeds first by the addition of the mercury salt to the amino group, *i. e.*, to form an ammonium salt. This ammonium salt then rearranges to a compound in which the mercuric radical is attached to carbon.<sup>5</sup>

From this theory of the mechanism of mercurization, one of the most logical deductions to be made is that, *of the aromatic amines only those which are capable of forming salts will mercurize*. Among other tests, one to which this deduction has been put was an attempt to mercurize trimethyl-phenyl-ammonium acetate, a compound in which the formation of a double salt with the mercuric acetate used is impossible. This com-

<sup>15</sup> Unpublished work of Kharasch, Lommen, and Jacobsohn.

<sup>16</sup> We found, however, that a hydrochloride of *p*-nitro-dimethylaniline could be prepared by passing dry hydrogen chloride into a benzene solution of the base.

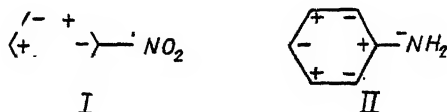
<sup>17</sup> Kharasch, Lommen, and Jacobsohn (unpublished work) have isolated the compound,  by treating an alcoholic solution of *m*-nitro-aniline with an aqueous solution of mercuric acetate.

<sup>18</sup> Klein, *Ber.*, 11, 743 (1878).

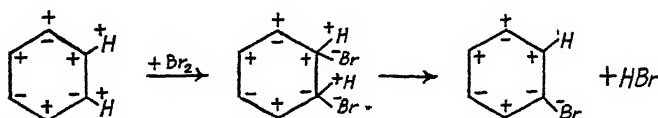
pound was not mercurized although a water suspension of dimethylaniline mercurizes within one or two minutes, with great evolution of heat.

The theory here advanced as to the mechanism of mercurization of aromatic amines adapts itself as already stated, quite readily to the explanation of the orientation of other groups upon substitution in the nucleus of aromatic amines.<sup>19</sup> Not only does it explain satisfactorily the cases of *ortho* and *para* substitution but, as will be shown later, it explains also the fact that a mixture of all three isomers is obtained when an aromatic amine is nitrated in conc. sulfuric acid solution, as well as the more recent observations of Vörländer<sup>20</sup> that, upon bromination and nitration, the quaternary ammonium salts yield only the *meta* derivative.

To explain these cases of *meta* substitution, Vorländer advances a theory of the benzene nucleus in which he assumes that the hydrogen atoms in the benzene molecule have positive tensions,<sup>21</sup> and that it is the tension within the nucleus which determines the position taken by the entering substituent. He assumes, further, that the nature of the tension on the group already substituted in the molecule exerts an influence on the arrangement of the tensions within the nucleus. Thus for nitrobenzene he assumes Structure I



while, for aniline, Structure II is assumed. Further, substitution takes place by absorption with the subsequent loss of a molecule of acid or water<sup>22</sup> thus:



<sup>19</sup> It is self-evident that this theory is applicable also to such rearrangements as those of hydrazobenzene, diazo-aminobenzene, the Fischer and Hepp, etc. It is to be noted, that, in all cases, where the rearranging compound is a weak base, the reaction must be carried out in anhydrous media to insure salt formation.

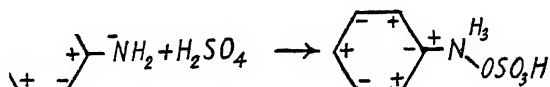
<sup>20</sup> Vorländer, *Ber.*, 52B, 263 (1919).

<sup>21</sup> In order to avoid committing himself to any theory as to the nature of valence, Vorländer uses the term "tension" and denotes the kind of tension by + and -. While he does not assume that they are electrical in nature, the properties assigned for them are such that, for the purpose of discussing substitution, there is little distinction to be made.

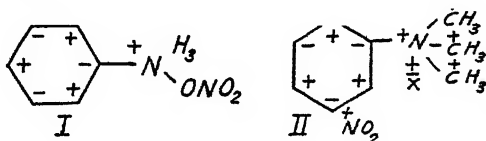
<sup>22</sup> It is rather peculiar that Vorländer does not take into account the fact that bromine is  $\text{Br}^+ - \text{Br}^-$ , unless by an error in print, since the existence of positive bromine has been proved conclusively. (W. A. Noyes, *THIS JOURNAL*, 23, 460 (1901); Stieglitz, *ibid.*, 23, 796 (1901); Walden, *Z. physik. Chem.*, 43, 385 (1903).



Vorländer makes the additional postulate, in order to explain the cases of *meta* substitution in aromatic amines, that, upon salt formation, there is a change in the tension throughout the molecule, *e. g.*, upon treating aniline with sulfuric acid, the following change is assumed to take place.



Such an assumption is entirely unwarranted. Not only are there no experimental facts upon which to base such an hypothesis, but the assumption made involves an upheaval taking place within the molecule, as well as a change of tension between the carbon and groups attached to it. Such a supposition as a change of tension would also demand that, in a compound such as aniline nitrate, analogous to aniline sulfate, the tension on the nitrogen bound to the phenyl group must be positive.



This compound should then, according to the views of Vorländer, give a *meta* derivative when dropped into conc. sulfuric acid. On the contrary, however, it gives only *o*- and *p*-nitro derivatives.<sup>23</sup> Similarly, the nitration of aromatic quaternary ammonium compounds demands, according to Vorländer, that the tension between the ammonium nitrogen and the carbon of the benzene nucleus be positive (II). This is hardly compatible with the fact that a water solution of the hydroxide of the compound (II) when evaporated gives a small quantity of trimethylamine and *m*-nitrophenol.<sup>24</sup> This theory must, therefore, be further modified if it is to be made to fit all the facts of substitution in aromatic amines.

Similarly, it has been necessary to make additional postulates to all previous theories in an attempt to build a workable theory of substitution. Yet, with all these postulates, none of the older theories can be made to fit all the facts of substitution. However, no new postulates need be made to the theory advanced by the present authors. Once it is assumed that all *ortho* and *para* substitution in the hydroquinoid nucleus of aromatic amines takes place through intermediate salt formation, it follows that, when such salt formation is impossible, as in the quaternary ammonium salts, substitution must take place in the *meta* position or, as in such special cases as that of mercurization, it is not accomplished at all.

<sup>23</sup> Bamberger, *Ber.*, 28, 400 (1895).

<sup>24</sup> Staedel and Bauer, *ibid.*, 19, 1939 (1885).

Not only does the theory advanced explain the case of *meta* substitution in the quaternary ammonium salts, but it explains also the fact that a mixture of all three isomers is obtained upon nitration of an aromatic amine in conc. sulfuric acid solution. It explains, further, the fact that the yield of the *meta* derivative increases with the amount of sulfuric acid used. Here it will be seen that an equilibrium mixture of both the amine and the ammonium salt exists in such a solution. Therefore, in such a mixture both types of substitution, that dependent upon intermediate compound formation, giving *ortho* and *para* derivatives, and the substitution of a salt yielding a *meta* derivative, are found. Again, as the volume of sulfuric acid is increased, the equilibrium will be shifted to form more of the sulfate, thus increasing the yield of the *meta* derivative.

Furthermore, the theory here advanced also offers an explanation of certain peculiar facts of rearrangement. For example, the rearrangement of  $\beta$ -phenyl-hydroxylamine<sup>25</sup> in alcoholic solution with hydrogen chloride as catalyst, gives not only *p*-amino phenetole but also *p*-chloro-aniline, the more strongly electro positive chlorine atom rearranging. The theory advanced predicts that N-substituted aromatic amines, when treated with a catalyst capable of being oxidized by the group already substituted in the molecule will yield a derivative having the more strongly electro positive group in the *para* position.

It will be seen, therefore, that the present theory explains from a single standpoint the rearrangement and substitution in the case of aromatic amines, without the necessity of any additional postulates. It is also far more adequate for the explanation of these facts and furnishes a more workable hypothesis than any of the other theories of substitution.

### Experimental Part.

#### Method used for Mercurization.

The method used for the preparation of the compounds herein described is, briefly, as follows. One mol of the compound to be mercurized was dissolved in a small volume of alcohol and boiled with an aqueous solution containing 0.9 mol of mercuric acetate, until a test portion gave no black precipitate of mercuric sulfide when treated with ammonium sulfide. This reaction mixture was filtered hot. Upon cooling, the acetate of the mercurized compound crystallized from the solution.

The filtrate from the above was treated with an aqueous solution of sodium chloride, whereupon the chloride of the mercury compound soon precipitated. The total yield of mercurized product calculated upon the basis of the mercuric acetate used, was almost quantitative.

An Attempt to Mercurize *p*-Nitro-dimethylaniline and *p*-Nitro-diethylaniline.—As stated in the theoretical part, several attempts were made to mercurize *p*-nitro-

<sup>25</sup> See, however, Stieglitz, *Am. Chem. J.*, 46, 327 (1911).

dimethylaniline, all of which met with failure. The method above outlined was used, as well as several other methods, none of which yielded a mercurized product. Similarly, attempts to mercurize *p*-nitro-diethylaniline were without success.

*o*-Nitro-*p*-Acetoxymercuri-dimethylaniline,  $(C_6H_5(1)N(CH_3)_2(2)NO_2(4)HgO_2C_2H_5)$ .—This compound was prepared from *o*-nitro-dimethylaniline and mercuricacetate. The reaction was completed after half an hour's boiling. The reaction mixture was filtered hot in order to remove the small amount of mercurous acetate formed in the reaction. It was then cooled and the precipitate collected on a filter. The precipitate was then washed with alcohol, and dried to constant weight *in vacuo* over sulfuric acid.

*Analyses.* Subs., 0.2759: dry  $N_2$ , 16.20 cc. (22° and 741 mm.). Subs., 0.2604:  $HgS$ , 0.1427. Calc. for  $C_{10}H_{12}O_4N_2Hg$ : N, 6.61;  $Hg$ , 47.23. Found: N, 6.63;  $Hg$ , 47.26.

The compound thus obtained is bright yellow; m. p. 160°. It is crystalline, and is soluble in the common organic solvents.

*o*-Nitro-*p*-Chloromercuri-dimethylaniline,  $(C_6H_5(1)N(CH_3)_2(2)NO_2(4)HgCl.H_2O)$ .—This compound was washed well with water to remove sodium chloride and finally with alcohol, and dried *in vacuo* over sulfuric acid to constant weight.

*Analyses.* Subs., 0.2635: dry  $N_2$ , 15.60 cc. (21.5° and 741 mm.). Subs., 0.3233:  $AgCl$ , 0.1096. Calc. for  $C_6H_5O_2N_2HgCl$ : N, 6.69;  $Cl$ , 8.46. Found: N, 6.71;  $Cl$ , 8.38.

The substance is red and amorphous. It is soluble in acetone and in boiling alcohol. It melts at 185°, with decomposition.

*m*-Nitro-*p*-Acetoxymercuri-dimethylaniline,  $(C_6H_5(1)N(CH_3)_2(3)NO_2(4)HgO_2C_2H_5)$ .—This preparation was obtained upon treating *m*-nitro-dimethylaniline with mercuric acetate. A half hour's boiling was sufficient to carry the reaction to completion. For analysis, the compound was dried to constant weight over sulfuric acid.

*Analyses.* Subs., 0.2924: dry  $N_2$ , 17.05 cc. (20° and 734 mm.). Subs., 0.2940:  $HgS$ , 0.1610. Calc. for  $C_{10}H_{12}O_4N_2Hg$ : N, 6.61;  $Hg$ , 47.23. Found: N, 6.56;  $Hg$ , 47.23.

The compound is obtained in the form of brilliant orange needles. It is soluble in the common organic solvents; m. p. 140°.

*m*-Nitro-*p*-Chloromercuri-dimethylaniline,  $(C_6H_5(1)N(CH_3)_2(3)NO_2(4)HgCl)$ .—This compound was obtained from the filtrate of the preceding preparation.

*Analysis.* Subs., 0.3438:  $AgCl$ , 0.1237. Calc. for  $C_6H_5O_2N_2HgCl$ :  $Cl$ , 8.84. Found: 8.90.

The compound is red and amorphous. It is soluble in acetone and in boiling alcohol. It melts at 220°, with decomposition.

*p*-Nitro-*o*-Acetoxymercuri-monomethylaniline,  $(C_6H_5(1)NH.CH_3(4)NO_2(2)HgO_2C_2H_5)$ .—This compound was prepared from *p*-nitro-methylaniline and mercuric acetate. The product obtained was extracted with ether in order to remove unchanged *p*-nitro-methylaniline, and the residue was recrystallized from alcohol. A dark red solid remained which was insoluble in alcohol, but the quantity was too small to be analyzed.

*Analyses.* Subs., 0.2585: dry  $N_2$ , 15.6 cc. (21° and 736 mm.). Subs., 0.2981:  $HgS$ , 0.1673. Calc. for  $C_9H_{10}O_4N_2Hg$ : N, 6.84;  $Hg$ , 48.82. Found: N, 6.79;  $Hg$ , 48.38.

The compound forms small yellow crystals melting at 197° with decomposition. It is soluble in acetone and in hot alcohol to which a few drops of glacial acetic acid have been added. When treated with a conc. potassium hydroxide solution, a brick-red compound is formed. Upon dilution, the compound again becomes yellow.

*p*-Nitro-*o*-Chloromercuri-monomethylaniline,  $(C_6H_3(1)N.H.CH_3(4)NO_2(2)HgCl.(H_2O))$ .—This compound is obtained from the filtrate of the preceding compound.

*Analysis.* Subs., 0.2972: AgCl, 0.1036. Calc. for  $C_7H_5O_2N_2HgCl$ : Cl, 8.75. Found: 8.62.

The compound is yellow and crystalline. It is soluble in acetone and in boiling alcohol. It melts at  $215^\circ$ , with decomposition.

The position of the mercury in this compound was determined by the method of Dimroth.<sup>26</sup> The acetate was treated with two equivalents of a solution of potassium permanganate. The product was then extracted with ether and the extract purified from alcohol; m. p.  $112-113^\circ$ . When mixed with 4-nitro-2,6-dibromo-monomethylaniline, prepared by the method of Blanksma,<sup>27</sup> the melting point was not lowered. The use of only one molecule of the bromine in solution yielded no definite compound. Since the position could not be thus in dispute the dibromo derivative was therefore isolated.

*p*-Nitro-*o*-Acetoxymmercuri-mono-ethylaniline,  $(C_6H_3(1)N.H.C_2H_5(4)NO_2(2)Hg.O_2.C_2H_3)$ .—This compound was prepared from *p*-nitro-mono-ethylaniline, and was purified from the unchanged raw material by recrystallization from alcohol.

*Analyses.* Subs., 0.2641: dry  $N_2$ , 15.7 cc. ( $24.5^\circ$  and 731 mm.). Subs., 0.3480:  $HgS$ , 0.1912. Calc., for  $C_{10}H_{12}O_4N_2Hg$ : N, 6.61; Hg, 47.23. Found: N, 6.56; Hg, 47.17.

It crystallizes from alcohol in small yellow crystals; m. p.  $183^\circ$ . It is also soluble in acetone. When treated with conc. potassium hydroxide solution, a brick-red compound is obtained. Dilution of the solution restored the original yellow color.

*p*-Nitro-*o*-Chloromercuri-mono-ethylaniline,  $(C_6H_3(1)N.H.C_2H_5(4)NO_2(2)HgCl.(H_2O))$ .—The compound was prepared in the usual manner. It is obtained in the form of an amorphous yellow solid; m. p.  $218^\circ$ , with decomposition. For analysis it was dried to constant weight over sulfuric acid.

*Analysis.* Subs., 0.4544: AgCl, 0.1573. Calc. for  $C_8H_{11}O_2N_2HgCl$ : Cl, 8.46; Found: 8.56.

It is soluble in acetone and in hot alcohol.

The position of the mercury in this compound was determined by the method used above for the corresponding methyl derivative. The melting point of the 4-nitro-2,6-dibromo-ethylaniline thus obtained was  $68-71^\circ$ . The melting point was not lowered when a mixture of the compound with known 4-nitro-2,6-dibromo-ethylaniline was used.

*p*-Nitro-*o*-Bromo-mono-ethylaniline,  $(C_6H_3(1)N.H.C_2H_5Br(4)NO_2)$ .—This compound was prepared by the addition of a solution of bromine in glacial acetic acid to a solution of an equivalent portion of *p*-nitro-mono-ethylaniline in the same solvent. After standing for about half an hour, the reaction mixture was diluted with water, and the precipitated compound collected on a filter. It was washed with water and a little alcohol. After crystallization from alcohol, the compound was dried to constant weight *in vacuo*. Yield, 90%.

*Analysis.* Subs., 0.2704: dry  $N_2$ , 26.50 cc. ( $17^\circ$  and 750 mm.). Calc. for  $C_8H_9O_2N_2Br$ : N, 11.44. Found: 11.39.

The compound crystallized from alcohol in beautiful long yellow prisms which are highly refractive; m. p.  $65^\circ$  to  $66^\circ$ . It is insoluble in water but soluble in all common organic solvents.

When an alcoholic solution of the compound is treated with conc. potassium hydroxide solution, the alcoholic layer assumes a red color. Upon evaporation of the alcohol, or upon dilution with water, the yellow compound is again obtained.

<sup>26</sup> Dimroth, *Ber.*, 35, 2033 (1902).

<sup>27</sup> Blanksma, *Rec. trav. chem.*, 31, 271 (1902).

*p*-Nitro-*o*-Dibromo-mono-ethylaniline,  $(C_6H_5(1)N.H.C_2H_5(2,6)Br_2(4)NO_2)$ .—This compound was prepared in the same manner as the above monobromo derivative, in this case, with two mols of bromine. For analysis the compound was crystallized from alcohol. Yield, 90%.

*Analysis.* Subs., 0.2761: dry  $N_2$ , 21.2 cc. ( $21^\circ$  and 744 mm.). Calc. for  $C_8H_8O_2N_2Br_2$ : N, 8.68. Found: N, 8.74.

This compound crystallized from alcohol in small yellow needles; m. p.  $75-76^\circ$ . It is insoluble in water, but soluble in all common organic solvents.

Upon treatment with a conc. potassium hydroxide solution, an alcoholic solution of the compound turns red. If the alcohol is evaporated, or the solution diluted with water, the color is restored to the original yellow.

*An Attempt to Mercurize Trimethyl-phenyl-ammonium Acetate.*—A solution of 0.5 mol of mercuric acetate was added to a solution of trimethyl-phenyl-ammonium acetate. Even after standing for two months at room temperature, no mercurized product could be isolated. The solution gave a heavy precipitate of mercuric sulfide when treated with hydrogen sulfide.

Upon boiling another portion of the solution for 24 hours, no change was observed. A heavy precipitate of mercuric sulfide was again obtained upon treatment with hydrogen sulfide.

### Summary.

1. A theory of the mercurization of aromatic amines has been advanced, postulating that mercurization is preceded by addition of a mercuric salt to the amino nitrogen, with the subsequent rearrangement of the mercury to the *ortho* or *para* position. This theory, without any additional postulates, has been shown to apply equally well to the introduction of other groups in the benzene nucleus in the case of aromatic amines.

2. This theory has been shown to apply also to rearrangements such as that of Fischer and Hepp, the nitro-amines, sulfamic acids, etc.

3. The limitations to other theories of substitution have been pointed out.

4. The preparation of mercury derivatives of *p*-nitro-methylaniline, *p*-nitro-ethylaniline, *o*-nitro-dimethylaniline, and *m*-nitro-dimethylaniline, and the preparation of *o*-bromo and *o,o*-dibromo-*p*-nitro-ethylanilines have been described.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## BENZYL ETHERS OF CARBOHYDRATES.

BY M. GOMBERG AND C. C. BUCHLER.

Received May 16, 1921.

In a previous communication<sup>1</sup> it was shown that benzyl esters could be prepared in good yields, and a pure condition, from benzyl chloride and the sodium salt of the corresponding acid dissolved in water; in aqueous solution, also, benzyl ethers, amines, benzonitriles, etc., were prepared. In testing further the applicability of this method of procedure, we have now studied the action of benzyl chloride upon carbohydrates.

Alkylation of carbohydrates had been limited for a time, since 1893, to E. Fischer's<sup>2</sup> method of making alkyl glucosides by the condensation of the carbohydrate and the alcohol through the agency of hydrochloric acid. Under these circumstances, the alkyl group becomes attached to the oxygen in the aldehydic or ketonic group, and can be readily separated by hydrolysis. Later, Maquenne<sup>3</sup> prepared  $\beta$ -methylglucoside by the action of methyl sulfate and sodium hydroxide on glucose. Purdie and Irvine<sup>4</sup> then showed that the hydrogen atoms in the four alcoholic hydroxyl groups also could be replaced by alkyl groups by the use of silver oxide and alkyl iodide. As was to be expected, the resulting ethers are not subject to the influence of hydrolyzing agents under ordinary conditions, and consequently they exceed greatly in stability the esters of the carbohydrates. Irvine and his co-workers have successfully methylated in this way a number of carbohydrates, partial alkylation occurring readily and complete alkylation being achieved by repeated treatment in several stages. The use of methyl sulfate for making methyl ethers of cellulose was described by Denham and Woodhouse in 1913.<sup>5</sup> In the same and in the following year appeared brief abstracts of patented processes<sup>6</sup> for methyl and ethyl cellulose ethers, using alkyl sulfates or halides. More recently Haworth<sup>7</sup> showed that not only cellulose, but various sugars can be alkylated through the agency of methyl sulfate and aqueous sodium hydroxide instead of the expensive materials as in the method of Purdie and Irvine. Since then, the methyl sulfate procedure alone, or that and followed by the more drastic treatment with methyl iodide and silver oxide, has been used by

<sup>1</sup> Gomberg and Buchler, *THIS JOURNAL*, **42**, 2059 (1920).

<sup>2</sup> Fischer, *Ber.*, **26**, 2400 (1893).

<sup>3</sup> Maquenne, *Bull. soc. chim.*, **33**, 469 (1905).

<sup>4</sup> Purdie and Irvine, *J. Chem. Soc.*, **83**, 1021 (1903).

<sup>5</sup> Denham and Woodhouse, *ibid.*, **103**, 1735 (1913); **105**, 2357 (1914).

<sup>6</sup> Lilienfeld, *J. Chem. Ind.*, **32**, 420 (1913); *Fr. pat.* 447,974, *C. A.*, **7**, 3839 (1913); *Brit. pat.* 12,854. Dreyfus, *J. Soc. Chem. Ind.*, **33**, 248 (1914); *Fr. pat.* 462,274.

<sup>7</sup> Haworth, *J. Chem. Soc.*, **107**, 8 (1915).

Denham and Woodhouse<sup>8</sup> on cellulose, by Haworth<sup>9</sup> on maltose and on cellobiose, by Irvine<sup>10</sup> on inulin, and by Karrer<sup>11</sup> on starch.

In addition there are several more recent patents.<sup>12</sup> All these patents make, of course, very broad claims for alkylating agents in general, but mention of specific examples is limited, so far as we are aware, to examples of methyl and ethyl ethers only, from cellulose and from starch. Benzyl ethers specifically we find mentioned only in Brit. pat. 149,320, "for carbohydrates of the general formula  $C_6H_{10}O_5$ ;" the abstract of this patent came into our hands after all the work described in this paper had been completed. Here, again, the working example described in this last patent is that of ethyl ethers.

Benzyl chloride, we find, lends itself exceedingly well to the alkylation of all classes of carbohydrates. No attempt was made for the present to ascertain the best conditions for the most complete alkylation, but merely to determine how general this reaction is. Methylglucoside, sucrose, lactose, inulin, dextrin, starch and cellulose all form benzyl ethers more or less readily. The general procedure was to dissolve, or suspend, the individual carbohydrate in water which contained enough sodium hydroxide to keep the solution alkaline throughout the whole period of reaction; benzyl chloride was added in the proportion of slightly more than 1 mol of the chloride for each hydroxyl group in the carbohydrate used, and the mixture well stirred. After the reaction was deemed to have been completed, the excess of benzyl chloride was removed by steam distillation, and the subsequent treatment was as described below, for the individual carbohydrates. For analysis, the purified products were dried at 100° for 6 to 10 hours.

### Experimental.

**Benzylation of Glucose.**—Several preliminary experiments with glucose gave unsatisfactory results, due no doubt to the detrimental action of the alkali upon the glucose.  $\alpha$ -Methylglucoside was then prepared by the method of E. Fischer, except that we used much less methyl alcohol and the latter contained only 10% of hydrogen chloride instead of being saturated with it. The glucose solution was allowed to stand until it ceased to reduce Fehling's solution, and a 50% yield of  $\alpha$ -methylglucoside was obtained.

When the glucoside was benzylated at 85° to 90°, an oil was obtained which was insoluble in water but soluble in benzene. The results of the

<sup>8</sup> Denham and Woodhouse, *J. Chem. Soc.*, 119, 77 (1921).

<sup>9</sup> Haworth, *ibid.*, 115, 809 (1919); 119, 193 (1921).

<sup>10</sup> Irvine, *ibid.*, 117, 1474 (1920).

<sup>11</sup> Karrer, *Helvetica chim. acta*, 3, 620 (1920).

<sup>12</sup> Lilienfeld, *C. A.*, 10, 2145 (1916); U. S. pat. 1,188,376. *C. A.*, 14, 3251 (1920); U. S. pat. 1,350,820. *C. A.*, 15, 436 (1921); Brit. pat. 149,320.

elementary analysis indicate that this must have been a mixture consisting largely of dibenzyl-methylglucoside with some higher benzylated products. The following procedure was employed in the separation of the reaction mixture into its components.

9.7 g. (1 mol) of methylglucoside, 12 g. (6 mols) of sodium hydroxide in 100 cc. of water, and 27.5 g. (4.4 mols) of benzyl chloride were heated with stirring at 90° to 95° for 6 hours. The excess of benzyl chloride was removed by steam distillation, the aqueous solution was decanted from the oily reaction product and worked up separately. The oil was then stirred up with 4 successive portions of 100 cc. each of hot water, in order to dissolve out any benzyl alcohol that might have been present. The residue was taken up in benzene, the solution dried with calcium chloride and the solvent completely removed. The oily product was then extracted several times with petroleum ether, b. p. 50° to 70°, which dissolved out about half of the material. On evaporation of the petroleum ether 1.5 g. of residue of a mobile consistency was obtained, which proved to be the completely benzylated product, tetrabenzyl-benzylglucoside. (II). The portion which did not dissolve in petroleum ether, also about 1.5 g., became a stiff paste, as it cooled. It proved to be dibenzyl-methylglucoside. (I).

*Analyses* I. Calc. for  $C_{17}H_{24}O_6(C_7H_7)_2$ : C, 67.37; H, 6.95. Found: C, 67.07; H, 6.81.

II. Calc. for  $C_{26}H_{34}O_6(C_7H_7)_5$ : C, 78.10; H, 6.65. Found: C, 78.25; H, 6.78.

The aqueous solution decanted from the mixture of the insoluble benzylated glucosides was examined for the presence of water-soluble products, and was found to contain 2.5 g. of unchanged methylglucoside, and 2 g. of benzylglucoside. The aqueous solution, after neutralization, was evaporated to dryness, extracted with 95% alcohol, the filtered alcoholic solution evaporated to dryness and again extracted with absolute alcohol; the latter was evaporated to dryness. The residual mixture was washed with benzene in order to remove any benzyl alcohol, and the two glucosides were separated from each other by means of acetone, which dissolved only the benzylglucoside and left behind a white crystalline mass, readily identified as the methylglucoside by its melting point, solubilities and composition. The product soluble in acetone was analyzed with the following result.

*Analysis*: Calc. for  $C_8H_{14}O_6(C_7H_7)$ : C, 57.78; H, 6.67. Found: C, 56.71; H, 6.89.

Thus, under the conditions described, the action of benzyl chloride upon methylglucoside yielded three products: benzylglucoside, dibenzyl-methylglucoside and tetrabenzyl-benzylglucoside.

The benzylglucoside showed the properties described for this compound by E. Fischer<sup>13</sup> who prepared it from benzyl alcohol and glucose. It was characterized by a bitter taste and was found to be soluble in water, alcohol, benzene, chloroform, ethyl acetate and acetone; insoluble in ether and in petroleum ether. It did not reduce Fehling's solution, but was readily hydrolyzed by 8% hydrochloric acid upon boiling the solution, and gave rise to a strongly reducing carbohydrate; it was soluble in conc. hydrochloric acid and was hydrolyzed by it in the cold.

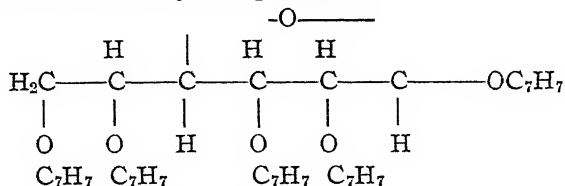
The substance of the composition of dibenzyl-methylglucoside was a semi-solid material, soluble in benzene and chloroform; it gave a cloudy

<sup>13</sup> Fischer, *Ber.*, 26, 2410 (1893).



solution with acetone and with ethyl acetate, was only slightly soluble in alcohol and in acetic acid, and insoluble in absolute ether and in petroleum ether. It was found to be without effect upon Fehling's solution; upon boiling with 8% hydrochloric acid for 1 hour it yielded a product still only little soluble in water, but strongly reducing.

Tetrabenzyl-benzylglucoside is the completely benzylated product. Assuming the usually accepted butylene oxide formula for the glucosides, the constitution of the benzylated product is,



This substance is an oil, as is the completely methylated  $\alpha$ -methyl-glucoside,<sup>14</sup> and is soluble in a greater variety of organic solvents than the partially benzylated compound, being soluble even in ether and in petroleum ether. It is not reducing, but becomes so upon boiling for an hour with dil. hydrochloric acid. In cold conc. hydrochloric acid it remains largely undissolved, and only after two days' standing does the solution show appreciable action upon Fehling's reagent.

**Benzylation of Sucrose.**—It was found difficult to judge the progress of the reaction in the case of sucrose, since the resulting products remain dissolved in the excess of the benzyl chloride.

One mol of sucrose, 8.8 mols of benzyl chloride and 12 mols of sodium hydroxide (10%) were heated for 4.5 hours at 85°. After steam distillation the residual gum was dissolved in a mixture of chloroform and benzene, the solution dried, and absolute ether added to the concentrated solution. The precipitated granular powder was rubbed up with fresh quantities of absolute ether, filtered, washed and dried. Analysis showed that the substance was a mixture of the monobenzyl derivative with higher alkylated products. In the next run, with materials in the same proportion as above, the heating was done at 100° for 3 hours and the reaction mixture was worked up in the same manner. The product consisted almost wholly of dibenzyl sucrose, containing 58.2% of carbon, and 6.1% of hydrogen. In the next experiment the action was more drastic. The mixture was heated for 4 hours at 100°, the aqueous layer was siphoned off and to the oil fresh benzyl chloride and sodium hydroxide solution were added. After further heating for 4 hours the mixture was worked up as described. There were no water-soluble benzyl sucroses formed; those insoluble in water were dissolved in chloroform. After evaporating all the chloroform the crude gummy product was resolved, on treatment with absolute ether, into two components: an insoluble white granular solid which proved to be dibenzyl sucrose, and a portion soluble in ether, an oil, which analyzed for a pentabenzyl sucrose. This oil, before analysis, was extracted several times with petroleum ether in order to remove any benzyl alcohol that might, perhaps, be present.

**Analyses.** Solid. Calc. for  $\text{C}_{12}\text{H}_{20}\text{O}_{11}(\text{C}_7\text{H}_7)_2$ ; C, 59.77; H, 6.51. Found: C, 59.73; H, 6.14.

Liquid. Calc. for  $\text{C}_{12}\text{H}_{17}\text{O}_{11}(\text{C}_7\text{H}_7)_5$ ; C, 71.21; H, 6.56. Found: C, 70.09; H, 6.53.

<sup>14</sup> Purdie and Irvine, *J. Chem. Soc.*, 83, 1080 (1903).

The dibenzyl and the pentabenzyl sucrose possess a most persistent bitter taste. Although they are practically insoluble in water, yet the supernatant aqueous layer acquires in a short time the intensely bitter taste. Neither of these compounds reduces Fehling's solution. On boiling with 8% hydrochloric acid small amounts of the substances are hydrolyzed and the solutions acquire reducing properties. In cold conc. hydrochloric acid the benzyl compounds dissolve partially. The solutions become dark colored and after 2 to 3 hours' standing show reducing properties, the dibenzyl derivative apparently hydrolyzing more readily than the pentabenzyl. The two compounds were found to be soluble in alcohol, acetic acid, chloroform, chlorohydrin, ethyl acetate, benzene, and nitrobenzene. The pentabenzyl was soluble also in ether and in acetone, while the dibenzyl sucrose was only slightly soluble in acetone and not at all in ether. Both were found to be insoluble in petroleum ether.

The benzyl sucroses furnish excellent examples of the influence of the benzyl group upon the physiological properties of substances. It is generally recognized that, in a substance possessing sweet taste, the entrance of a phenyl<sup>15</sup> or benzyl group into the molecule tends to decrease the sweetness, and it often inverts the taste completely from the sweet to the bitter. Methyl- and ethylglucosides,  $\alpha$ - and  $\beta$ -modifications, as well as the similar glucosides of other monoses, are all sweet; but with increase in weight of the alcohol molecule the taste begins to change, and the glucosides of benzyl alcohol, benzaldehyde, salicyl alcohol, of phenols—synthetic and natural glucosidic products—are in the great majority of instances bitter. Now, in the benzyl sucroses here described, the benzyl group can not be linked to an aldehydic or ketonic oxygen, since none such is present in sucrose, and yet these benzyl ethers compare well with quinine or picric acid in taste.

**Benzyl Dextrin.**—The dextrin used was a product known to have come from pure potato starch and was completely soluble in water.

One mol of dextrin, 3.5 mols of benzyl chloride and 4.5 mols of sodium hydroxide (9%), were heated at 80° to 85° for 4 hours, and treated in the usual manner. Upon addition of ether to the concentrated chloroform solution of the reaction mixture, from 16 g. of dextrin 18 gr. of the insoluble benzyl derivative was obtained. Elementary analysis gave results for carbon only slightly in excess of that required for a substance of the formula  $C_{12}H_{19}O_{10}C_7H_7$ . The benzyl compound obtained was a white amorphous tasteless powder, melting at about 208–10°. It was insoluble in water, acetone, ether; slightly soluble in benzene, and nitrobenzene. It swelled up in alcohol and ethyl acetate and with chloroform, chlorohydrin, and acetic acid gave colloidal transparent solutions which passed through filter paper with difficulty. It did not reduce Fehling's solution, was slowly hydrolyzed by dil. hot hydrochloric acid, or when in contact with the cold concentrated acid.

<sup>15</sup> G. Cohn, "Organische Geschmackstoffe," Franz Siemenroth, 1914, pp. 102, 243–266.

**Benzylation of Starch.**—The experiments were performed on two samples of starch of known origin, potato and corn starch. In each case the reaction temperature was  $85^{\circ}$  to  $90^{\circ}$ , the relative proportions of the reacting ingredients were the same as with dextrin, and yet the resulting products were not alike: potato starch took up one benzyl group for each  $C_{12}$  molecule, while corn starch took up two benzyl groups.

The crude gummy reaction product from potato starch, after thorough air drying, was dissolved in chlorohydrin, and the solution was diluted with chloroform and filtered through paper in a jacketed funnel. The benzyl compound was precipitated from its solution by the addition of ether, and the white powder was rubbed up in a mortar with several portions of fresh ether, filtered and dried. The yield was 8 g. of the powder from 8 g. of starch. The corn starch gave a crude product similar in appearance to that obtained from the potato starch. It was divided into portions: one portion was purified by solution in chlorohydrin and precipitation therefrom by means of ether, the second portion by solution in acetic acid and reprecipitation by ether. The yield was 20 g. of the benzyl compound from 16 g. of the corn starch.

*Analyses.* Potato starch. Calc. for  $C_{12}H_{19}O_{10}(C_7H_7)$ : C, 55.07; H, 6.28. Found: C, 55.85; H, 6.12.

Corn starch (chlorohydrin). Calc. for  $C_{12}H_{18}O_{10}(C_7H_7)_2$ : C, 61.92; H, 6.35. Found: C, 61.38; H, 6.38.

Corn starch (acetic acid). Calc. for  $C_{12}H_{18}O_{10}(C_7H_7)_2$ : C, 61.92; H, 6.35. Found: C, 60.43; H, 6.31.

The monobenzyl starch melted at  $200^{\circ}$  to  $203^{\circ}$ , the dibenzyl at  $203^{\circ}$  to  $205^{\circ}$ . Both were soluble in chlorohydrin and acetic acid, and insoluble in alcohol, acetone, ether, chloroform, benzene, nitrobenzene, ethyl acetate and benzyl benzoate. Filter paper, dipped into a solution of the benzyl starch becomes tough and water-proof when dry. With Fehling's solution the benzyl starches behave like benzyl dextrin.

**Inulin**, also, was benzylated in like manner as the starches, and the resulting product analyzed a little short for a substance of the formula  $C_{12}H_{19}O_{10}(C_7H_7)$ .

**Benzylation of Cellulose.**—Cellulose, unless previously subjected to one of the several so called "hydration" processes, was found to suffer but slight benzylation under the conditions as described for the other carbohydrates. It was found that benzylated cellulose was insoluble in Schweitzer's reagent, and this fact greatly facilitated the purification of the alkylated products.

(1) Absorbent cotton, subjected to previous hydration by means of zinc chloride and hydrochloric acid and, of course, carefully freed from these, was benzylated in the usual manner at  $90^{\circ}$  to  $95^{\circ}$ . The resulting product was still partially soluble in cuprammonium solution, and the elementary analysis indicated an extent of benzylation less than one benzyl group for each  $C_{12}$  molecule.

(2) Five g. of absorbent cotton was dissolved in Schweitzer's reagent and the solution allowed to stand overnight. The cellulose was precipitated by the addition of alcohol, and was thoroughly freed from copper. It was then digested for 12 hours with a solution of sodium hydroxide (11 g. of alkali in 73 cc. of water); 22 g. of benzyl chloride was added and the mixture was heated for 7 hours at  $90^{\circ}$  to  $95^{\circ}$ . After steam distillation, the product was thoroughly washed with water, alcohol and ether. The gray powder was then insoluble in cuprammonium solution, in chloroform, chlorohydrin, acetone, acetic acid, benzene and nitrobenzene.

*Analysis.* Calc. for  $C_{12}H_{19}O_{10}(C_7H_7)$ : C, 55.07; H, 6.28. Found: C, 54.34; H, 6.24.

(3) Five g. of absorbent cotton was converted into hydrocellulose by means of hydrogen chloride.<sup>16</sup> After completely washing out the acid from it, the material was digested for 3 hours with 50 cc. of 15% sodium hydroxide solution; then 10 cc. of water and 18 g. of benzyl chloride were added and the mixture was heated for 4 hours. The benzylated product was digested for several hours with cuprammonium solution, filtered, washed, digested in several changes of dil. hydrochloric acid, and washed with water, alcohol and ether. The benzylated product, amounting to 4 g., consisted of white very short fibres. Hydrocellulose is generally assumed to be a further degradation product of cellulose than the "cellulose hydrates." The composition of hydrocellulose is given as  $n(C_6H_{10}O_5) + H_2O$ ,  $n$  varying from 2 to 6,<sup>17</sup> and this relative composition is believed to be retained in the various derivatives of hydrocellulose.<sup>18</sup> For our purposes we may assume  $n$  equal to 4 and shall not be far from the truth.

*Analysis.* Calc. for  $2C_{12}H_{19}O_{10}(C_7H_7) \cdot H_2O$ : C, 53.90; H, 6.38. Found: C, 53.60; H, 6.58.

(4) Absorbent cotton was soaked in a 15% sodium hydroxide solution for 3 days, and then squeezed until the cotton retained about 3 times its weight of the alkaline solution. The alkali cellulose was heated for 5 hours at 100° with an excess of benzyl chloride. After steam distillation and preliminary purification, the product was digested for 2 days with cuprammonium solution and then purified as described above. Throughout the whole treatment the fibrous structure of the cotton was retained.

*Analysis.* Calc. for  $C_{12}H_{19}O_{10}(C_7H_7)$ : C, 55.07; H, 6.28. Found: C, 57.97; H, 6.37.

(5) More homogeneous products were obtained with filter-paper cellulose. Four g. of pure ashless paper, cut into small pieces, was soaked for 12 hours in 30 cc. of 20% sodium hydroxide solution; 45 cc. of water was then added and the mixture was heated for an hour at 90° to 95° with no apparent change. Seventeen g. of benzyl chloride was introduced and the heating continued. After 4 hours the paper began to change visibly, gathering into a clump. After another hour of heating, the mixture was worked up in the usual way, digested for a day in Schweitzer's reagent and purified.

*Analysis.* Calc. for  $C_{12}H_{19}O_{10}(C_7H_7)$ : C, 55.07; H, 6.28. Found: C, 55.38; H, 6.45.

(6) Filter-paper cellulose was subjected to a more energetic, two-stage, benzylation. Five g. of the paper was digested for 2 days at room temperature in a solution of 10 g. of sodium hydroxide in 30 cc. of water, 30 g. of benzyl chloride was added and the mixture was heated at 100° for 7 hours. After distillation with steam and thorough washing with water, alcohol and ether, the dried material weighed 6 g. A portion of this was saved for purposes of analysis, and the remaining 4.5 g. was subjected once more to the same treatment with alkali and benzyl chloride. It yielded, after washing with alcohol and ether, 5 g. of dry product which however proved to be not entirely homogeneous. On digestion with ethyl acetate most of it, but not all, went into solution and was reprecipitated from the clear filtrate, upon the addition of absolute alcohol, as a white, horny substance. The one-stage benzylated product was treated, before analysis, with cuprammonium solution.

*Analyses.* One-stage benzylation. Calculated for  $C_{12}H_{17}O_{10}(C_7H_7)_3$ : C, 66.67; H, 6.39. Found: C, 66.10; H, 6.41.

<sup>16</sup> Cross and Bevan, "Cellulose," Longmans Green and Co., 1918, pp. 54, 254.

<sup>17</sup> Meyer u. Jacobson, "Organische Chemie," Veit and Co., 1913, I, 2, p. 1044.

<sup>18</sup> Worden, "Technology of Cellulose Esters," Van Nostrand Co., 1916, VIII, p. 2541.

Two-stage benzylation. Calculated for  $C_{12}H_{16}O_{10}(C_7H_7)_4$ : C, 70.17; H, 6.58. Found: C, 69.74; H, 6.32.

It does not appear probable that the product showing the composition of tribenzyl cellulose is a mixture of di- and tetrabenzyl derivatives. The mono benzyl compound did not show signs of softening when heated to  $250^\circ$ , the tribenzyl substance melted at  $208^\circ$  to  $10^\circ$ , while the tetra benzyl compound softened at  $165^\circ$ , and melted at  $175^\circ$  to  $77^\circ$ . The tribenzyl substance appeared as fully insoluble in the various organic solvents as the monobenzyl derivative, while the tetrabenzyl cellulose proved soluble in chlorohydrin, chloroform, nitrobenzene, ethyl acetate, and was gelatinized by acetone.

The three benzyl derivatives do not reduce Fehling's solution. On treating with dilute acid, the monobenzyl and the tribenzyl compounds yield after 1 hour soluble reducing carbohydrates, while tetrabenzyl cellulose does not do so even after two hours' heating. None of the three substances is soluble in cold conc. hydrochloric acid, and the latter contains no reducing carbohydrates after 2 hours' contact with the products, and shows but a slight reduction after two days' standing.

#### Summary.

It has been shown that carbohydrates of all types are readily benzylated, and various benzyl ethers obtained are described. The benzylation reaction should prove useful in the further study of carbohydrates, just as alkylation by means of methyl sulfate has proven so preëminently fruitful in this field. Moreover, some of the benzyl ethers of the carbohydrates may prove, it is hoped, technically useful products because of their properties as colloid and plastic substances, particularly since benzyl chloride is relatively inexpensive and the group increases considerably the molecular weights of the carbohydrates to which it adds.

ANN ARBOR, MICH.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE BARRETT COMPANY.]

### THE QUANTITATIVE DETERMINATION OF PHENANTHRENE.<sup>1</sup>

BY ARTHUR G. WILLIAMS.\*

Received May 16, 1921.

The hydrocarbon phenanthrene has been the object of much research. It occurs in relative abundance in coal tar along with carbazole and anthracene, being isomeric with the latter. Much work has naturally been directed toward using it in making dyes and, indeed, many patents have been granted for dyes of which it forms a basis. Notable among such dyes is flavinduline. Further, the morphine alkaloids contain a phenanthrene nucleus, and this fact has been most potent in giving impulse to investiga-

<sup>1</sup> Read before the Dye Division of the American Chemical Society at the Rochester Meeting, April, 1921.

\* Died September 1, 1921.

tion of the chemistry of the hydrocarbon and of its derivatives. It will be clear that an adequate method of determining it is desirable.

In spite of the fact that the constituents of coal tar have interested chemists for many years past, there are comparatively few of these constituents for which accurate quantitative methods have been worked out,—methods comparable to that for anthracene, for example, and applicable in the presence of the usual accompanying substances. Thus we are still compelled to determine carbazole by first removing bases, then determining the remaining nitrogen and calculating it as carbazole. For naphthalene there is no chemical method at all comparable to that for anthracene, though the chemistry of the former early reached a high state of development. Highly accurate methods of determination then are almost everywhere lacking among the coal-tar constituents, even including benzene and toluene. It is not surprising, therefore, that for phenanthrene, which has only just begun to receive commercial development in this country, there should have been wanting an adequate mode of quantitative estimation.

**Historical.**—Record of essentially but one method of analysis appears in the literature.<sup>2</sup> In one variation the hydrocarbon is precipitated as the picrate from an alcoholic solution. The phenanthrene is then regenerated and washed with sulfuric acid to remove acridine. Allowance is made for the phenanthrene picrate remaining dissolved in the mother liquors. In the other variation<sup>3</sup> the hydrocarbon is precipitated as the picrate from xylene solution. An allowance is made for the amount of "rough picrate" remaining dissolved in the xylene mother liquor. A weighed portion of the precipitated "rough picrate" from the xylene is then recrystallized from 95% alcohol and a correction (20 g. of picrate for 750 cc. of 95% alcohol) applied in order to allow for the picrate remaining dissolved in the alcoholic mother liquors.

Küster<sup>4</sup> attempted the estimation of phenanthrene by conversion to the picrate by means of an aqueous solution of picric acid, but without success.

Obviously any attempt to determine phenanthrene by means of picric acid in the presence of the usual coal-tar accompaniments is seriously handicapped by two factors, (1) the relatively large solubility corrections that have to be applied, and (2) the fact that the most important anthracene-oil accompaniments of phenanthrene also form picrates of about the same order of solubility. Thus, for example, anthracene, carbazole, and fluorene all form picrates.

**Analysis of the Problem.**—The problem resolved itself, in view of the recorded chemistry of the compound, into (1) the quantitative oxidation of the hydrocarbon to the quinone, and (2) the quantitative estimation of the quinone produced.

<sup>2</sup> Anschütz and Schultz, *Ann.*, 196, 43 (1879).

<sup>3</sup> Lunge's "Coal Tar and Ammonia," Pub. D. Van Nostrand Co., 4th Ed., 1916, p. 643.

<sup>4</sup> Küster, *Ber.*, 27, 1104 (1894).

It was found convenient to solve the second part of the problem first in order to make it easy to follow progress in working out the first part.

### Experimental.

**Quantitative Determination of Phenanthraquinone.**—For this second aspect of the problem a solution lay already in view inasmuch as phenanthraquinone, as an *ortho*-diketone, forms generally well defined, rather insoluble compounds, azines, with *ortho*-diamines. 3,4-tolylene diamine was chosen as precipitant both because it forms with phenanthraquinone a well defined, sufficiently insoluble azine,<sup>5</sup> toluphenanthrazine, and because it is an easily obtainable *ortho*-diamine.<sup>6</sup> Moreover, the precipitation takes place very well in glacial acetic acid and since it was proposed to carry out the oxidation of phenanthrene also in glacial acetic solution, this fact was of great assistance. To be carried out, therefore, in connection with the second aspect of the problem, there remained for the most part only the obtaining of quantitative data regarding the precipitation, data by means of which progress in much of the search for a quantitative oxidant was followed.

*Experiment 1.*—One-fourth g. of phenanthraquinone (m. p. 203°) was dissolved in 25 cc. of glacial acetic acid. To the cold solution 0.60 g. of 3,4-tolylene-diamine was added. After standing in running tap water overnight, the precipitated toluphenanthrazine was filtered on a weighed Gooch crucible and washed with water. Yield, 0.3043 g., or 86.1%; m. p., 217° (uncorr.).

*Experiment 2.*—Another experiment in which only 0.28 g. of base was added and where the system stood in tap water only 30 to 40 min. resulted in a yield of 0.2979 g. of precipitate, or 84.5%. The precipitate was washed in this case, first with 50% acetic solution and then with water.

*Experiment 3.*—A third experiment was carried out as follows. 0.2500 g. of the quinone was dissolved in 25 cc. of glacial acetic acid in a 50cc. Erlenmeyer flask. 0.7407 g. of iodic acid (the oxidant for phenanthrene later found most suitable) was added and the solution was boiled under an air condenser for 2½ hours. No free iodine appeared. After standing overnight in tap water, the solution was filtered through a Gooch crucible into another Erlenmeyer flask and the residue of iodic acid washed with glacial acetic acid. Inasmuch as a slight sediment appeared in the filtrate (perhaps asbestos from the filter mat), the solution was distilled to less than 25 cc., then made up to 25 cc. and allowed to stand in running tap water overnight. The solution was again filtered, distilled to less than 25 cc. and made up again to 25 cc. 0.60 g. of base was added and, after standing in running tap water overnight, the precipitate was filtered off. It weighed 0.3026 g. an 85.6% yield; m. p., 215.5° to 216.6° (uncorr.).

The average yield in these three experiments is 85.4%, but 85.0% was taken for subsequent calculations as being within the experimental error in practical application. The theoretical weight of toluphenanthrazine from 0.2500 g. of phenanthraquinone is 0.3535 g. The solu-

<sup>5</sup> Hinsherg, *Ber.*, 18, 1228 (1885); *Ann.*, 237, 341 (1887).

<sup>6</sup> Gattermann, *Ber.*, 18, 1483 (1885); Kleemann, *ibid.*, 19, 336 (1886); Beilstein and Kuhlberg, *Ann.*, 158, 351 (1871).

bility of toluphenanthrazine in 25 cc. of glacial acetic acid is, for practical purposes, represented by  $(100 - 85 =) 15\%$  of 0.3535 g., or 0.0530 g. This latter weight, then, since precipitation was always performed in 25 cc. of solution, was always added as a correction to the weight of the azine precipitated.

The three experiments described above further indicate that the amount of base added is without material influence on the result and that iodic acid does not destroy phenanthraquinone under the conditions.

Another base, 1-ethoxy-3,4-diaminobenzene<sup>7</sup> was later tried and found to precipitate 91.3% of 0.2500 g. of phenanthraquinone under conditions as above described. Washing in this case was first performed with 25 cc. of a 50% acetic acid solution saturated with *p*-ethoxy-phenanthrazine,<sup>8</sup> the product precipitated, and finally with water. This diamine was not further experimented with, however, inasmuch as considerable data were already at hand based on the use of 3,4-tolylenediamine.

**The Quantitative Oxidation of Phenanthrene.**—Many substances were tried in the course of the search for a quantitative oxidant for phenanthrene. Among the substances which, judging in some cases only by the appearance of yellow color, resulted in the formation of phenanthraquinone when boiled with a glacial acetic acid solution of phenanthrene, were lead dioxide, manganese dioxide (upon the addition of a few cubic centimeters of 1-1 sulfuric acid), hydrogen peroxide, potassium chlorate, potassium bromate, potassium iodate, and iodic acid. Chromic acid was not experimented with since it is known to have a destructive action on phenanthraquinone. The search finally narrowed down to the potassium halates and from these to iodic acid, which alone was found to be suitable. Potassium bromate was found to be much quicker in action than iodic acid but it also had a destructive effect on phenanthraquinone. For example, after boiling a solution of 0.2500 g. of the quinone in 25 cc. of glacial acetic acid for 2½ hours with 0.80 g. of potassium bromate, but 59.7% of the quinone was precipitable as toluphenanthrazine.

Experiments according to the Höchst test with iodic acid were carried out using a sample of phenanthrene (A) containing 8.4% of anthracene<sup>9</sup> and no doubt other impurities, although it was a pure white material of excellent appearance. In each of these experiments a solution of 0.2500 g. of the hydrocarbon in 25 cc. of glacial acetic acid, contained in a 50cc. Erlenmeyer flask, was boiled with 0.74 g. of iodic acid under an air condenser for the time specified. Each flask was then allowed to stand in running tapwater overnight, after which the excess of iodic acid

<sup>7</sup> Autenrieth and Hinsberg, *Arch. Pharm.*, **229**, 456 (1891).

<sup>8</sup> Autenrieth and Hinsberg, *Ber.*, **25**, 497 (1892).

<sup>9</sup> Essentially as described in Lunge's "Chem.-tech. Untersuchungsmethoden," Julius Springer, Berlin, 4th Edition, Vol. II, p. 740.



was filtered through a Gooch crucible (mat dry, or wet with acetic acid) into another Erlenmeyer flask (a 100cc. flask is most conveniently used) and washed with glacial acetic acid. The filtrate was evaporated to slightly less than 25 cc. and then made up to exactly 25 cc. by comparison with a similar flask containing 25 cc. of water. When the contents of the flask were cool, 0.60 g. of the base was added. After standing overnight, the precipitate was filtered on a weighed Gooch crucible and washed first with 25 cc. of 50% acetic acid and then with water. The solubility correction of 0.0530 g. was added in each case and the percentage of phenanthrene calculated. The factor for the conversion of toluphenanthrazine to phenanthrene is 0.6052.

The results of five experiments are tabulated as follows.

Expt.	Boiling time. Hours.	Wt. of precipitate. G.	Phenanthrene indicated. %.	Remarks.
4	0.5	0.0838	33.1	m. p. of ppt. 213.5°. (uncorr.)
5	2.0	0.2927	83.7	m. p. of ppt. 213°-213.5°. (uncorr.)
6	2.5	0.2949	84.2	
7	2.5 or 3.5	0.2958	84.4	Boiling time probably 2½ hrs.
8	3.0	0.2924	83.6	

The results of four similar experiments with a much purer phenanthrene, (B), melting at 99.6° follow. They differ only in that 0.75 g. of iodic acid and 1.00 g. of base were used and in that the 50% acetic acid wash solution was saturated with toluphenanthrazine, variations having little or no effect on the results.

Expt.	Boiling time. Hours.	Wt. of precipitate. G.	Phenanthrene indicated. %.
9	2.5	0.3359	94.1
10	2.5	0.3367	94.2
11	3.0	0.3356	94.1
12	3.75	0.3352	94.0

The preceding nine experiments, together with Expt. 3, show that phenanthraquinone in acetic acid solution is not attacked by iodic acid and they indicate that 2½ hours' boiling results in a quantitative oxidation of the phenanthrene, inasmuch as longer boiling times do not cause any further alteration in the phenanthrene content found.

That a quantitative oxidation of phenanthrene had been attained was further shown by the results of analyses of mixtures of the 84.2% phenanthrene (A), with a high purity anthracene (C), with an anthracene of lower grade (D), and with an analyzed crude phenanthrene (E). Sample C melted at 216° and analyzed 97.05% anthracene; Sample D was a technical product of 88.7% purity, and Sample E analyzed 68.4% phenanthrene (see Expts. 18 and 19). The following tabulation and remarks present the results of these experiments and detail any varia-

tions in procedure. The duration of oxidation in each experiment was  $2\frac{1}{2}$  hours. 0.60 g. of base was used each time.

Expt.	Composition of sample.	Wt. of $\text{HIO}_3$ . G.	Wt. of precipitate. G.	Phenanthrene. Found. %.	Calc. %.
13	0.2500 g. of Anth. C +0.2500 g. of Phen. A	1.5	0.2744	39.6	42.1
14	"	1.5	0.2771	39.9 <sup>a</sup>	42.1
15	0.8000 g. of Anth. C +0.2000 g. of Phen. A	2.0	0.2110	16.0 <sup>a</sup>	16.8
16	0.1250 g. of Anth. D +0.1250 g. of Phen. A	0.75	0.1348	45.5	42.1 + x
17	0.1250 g. of Phen. E +0.1250 g. of Phen. A	0.75	0.2634	76.6	76.3

<sup>a</sup> The somewhat low results may indicate the desirability of longer oxidation time in the case of materials high in anthracene.

REMARKS.—*Expts. 13, 14, and 15:* Oxidized in 50 cc. of glacial acetic acid; let stand 48 hours in running water; filtered off precipitated anthraquinone, washing with glacial acetic acid; distilled to 20 cc.; let stand overnight in running water; filtered off slight brownish deposit of impure anthraquinone, washed with glacial acetic acid; distilled to 25 cc.; cooled; added base; let stand overnight in running water.

*Expt. 16:* Oxidized in 25 cc. of glacial acetic acid; let stand overnight in running water; filtered off the precipitated anthraquinone, washing with glacial acetic acid; distilled to about 18 cc.; let stand overnight in running water; filtered, washing with glacial acetic acid; distilled to 25 cc.; cooled; added base; let stand in running water overnight.  $x = \%$  of phenanthrene from Sample D, doubtless not more than a few per cent.

*Expt. 17:* Similar to 16 except that there was but one distillation.

Anthracene also is oxidized to the quinone by iodic acid, hence the necessity of the procedure followed in the preceding five experiments directed toward removing anthraquinone. This separation is possible because of the very considerably lower solubility of anthraquinone in glacial acetic acid as compared with phenanthraquinone.

Both potassium bromate and iodic acid in glacial acetic acid are excellent oxidants for anthracene. Boiling 0.2500 g. of a 97.0% anthracene in 25 cc. of glacial acetic acid for 5 minutes with 0.70 g. of potassium bromate resulted in an oxidation of 74.1% of the anthracene. Boiling 1.0000 g. in 50 cc. for 20 minutes with 2.5 g. of potassium bromate resulted in an oxidation of 92.8% and 89.8% (2 samples). Boiling 1.0000 g. in 50 cc. for  $2\frac{1}{2}$  hours with 3.00 g. of iodic acid resulted in an oxidation of 98.4% and 98.3% of the anthracene (2 samples). Following oxidation, the determination of the anthraquinone produced was accomplished as in the Höchst procedure for anthracene. Potassium bromate and iodic acid are probably quantitative oxidants for this hydrocarbon.

**Examples of Application of the Method.**—The phenanthrene was determined on three specimens of crude phenanthrene. The first was the material (E) referred to above, the second (F) was essentially the

phenanthrene fraction from a column distillation (plant scale) of an anthracene oil and was an oily solid, while the third (G) was the press-cake obtained from Sample F by pressing in a letter-press between folds of filter paper. 0.60 g. of base and 0.74 g. of iodic acid were used in each determination.

Expt.	Material. G.	Wt. of precipitate. G.	Phenanthrene. %.
18	0.2500 (E)	0.2290	68.26
19	"	0.2304	68.61
20	0.2500 (F)	0.2097	60.8
21	"	0.2151	61.9
22	0.2500 (G)	0.2643	76.8
23	"	0.2589	75.5

REMARKS.—*Expts. 18 and 19:* Oxidized in 25 cc. glacial acetic acid; cooled; filtered, washing with glacial acetic acid; distilled to 25 cc.; cooled; added base; let stand overnight; filtered, washed with 25 cc. of 50% acetic acid saturated with toluphenanthrazine, and with water.

*Expts. 20 and 21:* Oxidized in 20 cc. of glacial acetic acid; let stand overnight; filtered, washed with glacial acetic acid; distilled to 18–20 cc.; let stand overnight; filtered, washed with glacial acetic acid; distilled to 25 cc.; cooled; added base; finished as for No. 18.

*Expt. No. 22:* Same as for Expts. 20 and 21, except that material received but one distillation.

*Expt. No. 23:* Same as for Expts. 20 and 21.

In the hands of two other persons, Sample F gave the following results: 60.8%, 58.4%, average 59.6%; 61.2%, 60.3%, average 60.8%. These results represented their first experience with the method.

**Material Suited to Analysis.**—The method of analysis for phenanthrene employed in the preceding experiments is, in general, suitable for mixtures of anthracene-oil hydrocarbons 30% or higher in phenanthrene, containing less than 10% of carbazole, and containing no large amounts of the anthracene-oil constituents boiling above 360°. Cruder material requires preparation directed toward lowering the carbazole content and toward removing the high-boiling constituents. The method is best suited for crude and refined phenanthrenes and phenanthraquinones. It has been applied with satisfactory results directly to the phenanthrene range of distillates from a plant column distillation of anthracene oil.

Carbazole, if present in amounts exceeding perhaps 10%, interferes in the determination of phenanthrene. An oxidation product apparently is formed. This product is colored and behaves rather like a quinone. It will be further investigated. Fluorene does not interfere since it is not attacked. Acenaphthene, also, does not interfere because the quinone, if formed, gives a rather soluble azine. Moreover, acenaphthene is not likely to occur in any considerable proportion along with phenanthrene. In any event, the two hydrocarbons can be separated by distillation. Some

of the high-boiling coal-tar constituents interfere and a crude anthracene cannot be directly analyzed. Anthracene does not interfere since the anthraquinone formed may be filtered off from a smaller volume than that in which it is intended to precipitate the phenanthraquinone.

### Formal Analytical Procedure.

For materials containing 30% or more of phenanthrene, weigh out a 0.2500g. sample into a 50cc. Erlenmeyer flask. Add 0.75 g. of iodic acid and 20 cc. of glacial acetic acid. Fit a plain 90cm. air condenser to the flask and boil for  $2\frac{1}{2}$  hours at such a rate that the ring of iodine which usually condenses in the tube stands about 60 cm. from the flask. Cool, preferably for several hours, especially if anthraquinone separates, and then filter with gentle suction into a 100cc. Erlenmeyer flask through a Gooch crucible. A glass filter funnel (so-called carbon filter) is best used to hold the crucible. The oxidation mixture should be so slowly poured into the crucible that only a minimum amount of wash liquid need be used. Wash with glacial acetic acid. Fit the flask to a small empty Hempel distilling tube and distil to a volume *slightly* less than 25 cc. Some iodine will be carried over. By treating a portion of the distillate with a sodium thiosulfate solution, the color of the iodine may be removed in order to obtain assurance that no quinone has been carried over. Remove the Erlenmeyer flask and while the liquid is still warm make the volume (by comparison) up to 25 cc., as exactly as possible, with glacial acetic acid. Cool. Add 1.00 g. of 3,4-tolylene-diamine and swirl the flask until it has dissolved. A darkening, due to the action of iodine, will occur when the diamine is added. Set the flask in running water (at about 20°) overnight. Filter through a weighed Gooch crucible, using 25 cc. of a 50% glacial acetic acid solution saturated with toluphenanthrazine in transferring the precipitate and in the first part of the washing on the filter. Finally, wash with 200 cc. of cold water, dry the precipitate, and weigh. To the weight of the toluphenanthrazine add 0.0530 g., the weight of toluphenanthrazine remaining dissolved in the mother liquor. Multiply the sum by 0.6052, the factor for the conversion of toluphenanthrazine to phenanthrene, and calculate the percentage of the latter.

If the anthracene content exceeds a certain percentage (probably not under 15%, but perhaps considerably higher) anthraquinone may crystallize on cooling after oxidation. This will not interfere unless it is necessary to use so much acetic acid for washing that enough anthraquinone is dissolved to come down again when the volume is reduced to 25 cc. If, following distillation, it should crystallize out on cooling and making the volume up to 25 cc., further distillation to about 20 cc., cooling, refiltration, redistillation, etc., will be necessary.

With certain materials low in phenanthrene, it is practicable to weigh out 0.5000g. samples and oxidize in 50 cc. of glacial acetic acid with 1.50 g. of iodic acid. In such cases, the first distillation is carried to less than 25 cc. and the solution is allowed to cool and stand. It is then filtered again, distilled, etc., and precipitation is performed in 25 cc., as usual.

### The Qualitative Determination of Phenanthrene.

Phenanthrene may be very conveniently determined qualitatively in the following manner. Oxidize the material to be tested as for quantitative determination. Cool; filter; pour the filtrate into water; filter; wash with water. Warm the residue with conc. sodium hydrogen sulfite solution. Filter and transfer the filtrate to a small separatory funnel. Wash with one or two portions of carbon tetrachloride to remove any accompanying hydrocarbons. Add a small portion of fresh carbon tetrachloride and acidify with hydrochloric acid containing ferric chloride to prevent the reduction of the liberated phenanthraquinone. Collect the quinone in the carbon tetrachloride and, first drying the spout of the funnel, draw off the carbon tetrachloride, which contains the quinone, and test by the reaction of Hilpert and Wolf.<sup>10</sup> The solution of the quinone is heated to boiling and there are added a few drops of a solution of 1 volume of antimony pentachloride in 2 volumes of carbon tetrachloride. A purple-red precipitate indicates phenanthraquinone and hence phenanthrene. Anthraquinone, which gives a cinnabar-red color with this reagent, cannot interfere because it would not be present, nor can acenaphthenequinone because it gives an apple-green precipitate. Fluorenone, which gives an orange precipitate, turning to reddish-orange, also would not be present.

### Summary.

Phenanthrene may be determined quantitatively by oxidation in glacial acetic acid by means of iodic acid to phenanthraquinone followed by precipitation of the quinone produced by means of 3,4-tolylene-diamine.

A procedure for the qualitative detection of phenanthrene is described.

NEW YORK, N. Y.

<sup>10</sup> Hilpert and Wolf, *Ber.*, 46, 2217 (1913).

[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO.]

**FRIEDEL AND CRAFTS' REACTION. THE CARBOMETHOXY-BENZOYL CHLORIDES WITH AROMATIC HYDROCARBONS AND ALUMINUM CHLORIDE.**

BY MAURICE E. SMITH.

Received May 18, 1921.

Roser<sup>1</sup> obtained the amyl ester of benzoyl-formic acid from the acid chloride of mono-amyl oxalate, benzene and aluminum chloride. This preparation suggested the use of the acid chlorides of the mono-alkyl esters of the phthalic acids for the preparation of various keto acids.

The isophthalic acid and the terephthalic acid were prepared by the oxidation of commercial xylene, which had been fractionated with a 150cm. column, by Professor Kenrick in this laboratory. It was found that the fraction boiling at 138.2° to 138.4° gave the largest yield of terephthalic acid.

**Oxidation of the Xylene.**—Fifty g. of xylene, b. p. 138.2° to 138.4°, 5 liters of water and 30 g. of sodium hydroxide were heated to 90° in a 10-liter can which had a tight-fitting cover containing openings for condenser, mechanical stirrer and thermometer. All the openings were made steam tight. To the mixture was added 300 g. of potassium permanganate in 4 equal portions at half-hour intervals. After 19 hours' heating at 85° to 95° the solution was decolorized with methyl alcohol, cooled, filtered and the filtrate acidified. The precipitate dried at 110° weighed 60 g.

**Separation of the Acids.**—This product was found to be practically free from phthalic acid which is soluble 0.58 g. in 100 g. of water at 20°. The isophthalic acid and terephthalic acid were separated by means of their barium salts. The solubility of barium terephthalate and barium isophthalate, determined by evaporating a saturated solution and drying the residue at 200° for 8 hours, was found to be approximately 0.5 g. and 14.0 g. respectively in 100 g. of water at 20°. Fittig<sup>2</sup> using this method boiled the acids with barium carbonate but this is not convenient when using large quantities.

Sixty g. of the mixed acids was made into a paste with water and warmed with 125 cc. of conc. ammonia on a water-bath for 20 minutes; more water was then added to dissolve the ammonium salts, and the solution was boiled to expel the excess of ammonia. When nearly neutral, the volume was made up to 350 cc. and a hot solution of 40 g. of barium chloride in 70 cc. water added. After shaking for one hour and standing for 12 hours the barium terephthalate was filtered off, washed, and digested on a water-bath for 6 hours with 100 cc. of 15 % hydrochloric acid; yield

<sup>1</sup> Roser, *Ber.*, 14, 940 (1881).

<sup>2</sup> Fittig, *Ann.*, 153, 269 (1870).

of terephthalic acid 11.5 g. The combined filtrates were acidified affording 47 g. of isophthalic acid.

Further purification of the acids was effected by recrystallization of the dimethyl esters. Twenty g. of isophthalic acid and 150 cc. of methyl alcohol saturated with hydrogen chloride on standing for 36 hours gave 19 g. of dimethyl isophthalate, m. p.  $66^{\circ}$  to  $67^{\circ}$ . Ten g. of terephthalic acid boiled for 7 hours with 150 cc. of methyl alcohol and 15 cc. of conc. sulfuric acid gave 8 g. of dimethyl terephthalate, m. p.  $141^{\circ}$ .

***o*-Carbomethoxy-benzoyl Chloride with Benzene and Aluminum Chloride.**—Six g. of *o*-carbomethoxy-benzoyl chloride was dissolved in 80 cc. of benzene, cooled to  $10^{\circ}$ , and 10 g. of aluminum chloride added gradually with shaking. After standing for one hour at room temperature the mixture was kept at  $80^{\circ}$  for 7 hours and then poured into 100 cc. of 10% hydrochloric acid. After distilling off the benzene the ester was hydrolyzed with alcoholic potassium hydroxide, water was added and the solution was acidified with hydrochloric acid. The precipitate when recrystallized from ethyl alcohol gave 4.7 g. of *o*-benzoylbenzoic acid.

***m*-Carbomethoxyl-benzoyl Chloride with Benzene and Aluminum Chloride.**—Five g. of *m*-carbomethoxy-benzoyl chloride was dissolved in 90 cc. of benzene and 9 g. of aluminum chloride added. The mixture was kept at  $45^{\circ}$  to  $50^{\circ}$  for 5 hours and then at  $80^{\circ}$  for 7 hours. After hydrolysis of the ester and recrystallization from dilute alcohol the yield of *m*-benzoyl-benzoic acid, m. p.  $161$ – $162^{\circ}$ , was 3.9 g.

Silver salt. Calc. for  $C_{14}H_9O_3Ag$ : Ag, 32.4. Found: 31.9.

This acid had previously been prepared by Doebner<sup>3</sup> from benzoic anhydride, benzoyl chloride and zinc chloride, by Ador<sup>4</sup> as a by-product in the preparation of isophthalophenone, and by Senff<sup>5</sup> who oxidized benzyl-toluol. None of these methods give nearly as good a yield as was obtained above.

***p*-Carbomethoxy-benzoyl Chloride with Benzene and Aluminum Chloride.**—Five g. of *p*-carbomethoxy-benzoyl chloride, 50 cc. of benzene and 8.5 g. of aluminum chloride were heated at  $45^{\circ}$  to  $50^{\circ}$  for 5 hours and then on a boiling water-bath for 5 hours. After hydrolysis of the ester the *p*-benzoyl-benzoic acid was separated from terephthalic acid by dissolving in alcohol and recrystallized by the addition of water, m. p.  $194^{\circ}$ ; yield, 4 g; terephthalic acid recovered, 2 g.

One g. of the acid dissolved in thionyl chloride and added to methyl alcohol gave after recrystallization from methyl alcohol 1 g. of methyl *p*-benzoyl-benzoate, m. p.  $106$ – $107^{\circ}$ .

<sup>3</sup>Doebner, *Ber.*, 14, 647 (1881).

<sup>4</sup>Ador, *ibid.*, 13, 320 (1880).

<sup>5</sup>Senff, *Ann.*, 220, 236 (1883).

***o*-Carbomethoxy-benzoyl Chloride with Toluene and Aluminum Chloride.**—Five g. of *o*-carbomethoxy-benzoyl chloride, 50cc. toluene, and 8.5 g. of aluminum chloride were heated at 45° to 50° for 5 hours and then on a boiling water-bath for 7 hours. After addition of hydrochloric acid and removal of the toluene the reaction product was separated by the addition of ether, hydrolyzed with alcoholic potassium hydroxide and recrystallized from dil. alcohol, m. p. 96–100°; dried in a vacuum at 80°, m. p. 138° to 40°. The acid was fused with potassium hydroxide for 20 minutes at 200° and gave a mixture of benzoic acid and *p*-toluic acid. As it was not easy to separate these acids the mixture was boiled for 3 hours with alkaline permanganate solution, acidified and the product esterified with methyl alcohol. The ester recrystallized from alcohol melted at 140°. This identifies it as dimethyl terephthalate and identifies the product of hydrolysis as *p*-toluic acid. The original acid is, therefore, *p*-toluyl-*o*-benzoic acid. This acid has been prepared from phthalic anhydride, toluene and aluminum chloride by Limpricht<sup>6</sup> and others.

***m*-Carbomethoxy-benzoyl Chloride with Toluene and Aluminum Chloride.**—Five g. of *m*-carbomethoxy-benzoyl chloride was dissolved in 60 cc. of benzene and, after cooling the solution to 10°, 9 g. of aluminum chloride was added gradually. After standing at room temperature for one hour, the mixture was heated on a water-bath for 10 hours. The product was hydrolyzed with alcoholic potassium hydroxide and the acid obtained was recrystallized from hot methyl alcohol. Yield, 4.0 g.; m. p. 172°.

Silver salt. Calc. for  $C_{15}H_{11}O_3Ag$ : Ag, 31.1. Found: 30.8.

On fusion with potassium hydroxide and oxidation of the acid product with potassium permanganate, terephthalic acid, identified by its methyl ester, was obtained. The method of preparation and the product of hydrolysis identify the product of this reaction as *p*-toluyl-*m*-benzoic acid, not previously described.

One g. of *p*-toluyl-*m*-benzoic acid was dissolved in thionyl chloride, the excess of thionyl chloride removed and 25 cc. of methyl alcohol added. After the reaction ceased the solution was poured into cold water and the ester recrystallized from methyl alcohol, m. p. 108°. Yield of methyl *p*-toluyl-*m*-benzoate, 0.9 g.

***p*-Carbomethoxy-benzoyl Chloride with Toluene and Aluminum Chloride.**—Five g. of *p*-carbomethoxy-benzoyl chloride, 60 cc. of toluene, and 9 g. of aluminum chloride were heated for 9 hours at 40–50° and then for 2 hours on a boiling water-bath. After washing the reaction product with dil. sodium hydrogen carbonate solution, it was hydrolyzed with alcoholic potassium hydroxide and the acid recrystallized from methyl alcohol; m. p. 228°; yield 4.4 g. The methyl ester was prepared; m. p.

<sup>6</sup> Limpricht, *Ann.*, 299, 300 (1898).



126°. *p*-Toluyyl-*p*-benzoic acid had previously been prepared by Limp-richt<sup>7</sup> by oxidizing *p,p*-ditolyl ketone.

*o*-Carbomethoxy-benzoyl Chloride with *m*-xylene and Aluminum Chloride.—Five g. of *o*-carbomethoxy-benzoyl chloride and 50 cc. of *m*-xylene were cooled to 10° and 8.5 g. of aluminum chloride was added gradually. After the initial reaction had ceased the mixture was warmed on a water-bath until hydrogen chloride ceased to come off. After acidification and removal of the *m*-xylene the reaction product was extracted with chloroform, hydrolyzed with alcoholic potassium hydroxide and recrystallized from benzene as fine needles; m. p. 139–140°; yield, 3.5 g.

Silver salt. Calc. for  $C_{16}H_{13}O_3Ag$ : Ag, 29.9. Found: 30.2.

On fusion of the acid with potassium hydroxide for 30 minutes at 160° to 170°, and sublimation of the acid product, benzoic acid and 2,4-dimethyl-benzoic acid, m. p. 124° to 126°, were identified. The acid is therefore 2,4-dimethyl-benzoyl-*o*-benzoic acid and is identical with the acid prepared by Meyer<sup>8</sup> from phthalic anhydride, *m*-xylene and aluminum chloride. Meyer gave no melting point.

*m*-Carbomethoxy-benzoyl Chloride with *m*-xylene and Aluminum Chloride.—Five g. of *m*-carbomethoxy-benzoyl chloride, 40 cc. of *m*-xylene and 8.5 g. of aluminum chloride were kept at 20° for 5 hours and then on a boiling water-bath for 6 hours. After acidification and removal of the *m*-xylene the reaction product was extracted with chloroform, washed with dil. sodium hydrogen carbonate solution, hydrolyzed with alcoholic potassium hydroxide and acidified; yield of crude acid, 6.0 g. Recrystallized from hot methyl alcohol the acid melted at 168°; yield, 4.0 g.

Silver salt. Calc. for  $C_{16}H_{13}O_3Ag$ : Ag, 29.9. Found: 30.0.

On fusion of the acid with potassium hydroxide for 20 minutes at 170° to 80° and sublimation of the acid products the sublimate contained benzoic acid and 2,4-dimethyl-benzoic acid, m. p. 126°, and the residue from the sublimation was isophthalic acid, identified by the formation of its methyl ester. The greater part of the acid decomposes into isophthalic acid and *m*-xylene, but part of it gives benzoic acid and 2,4-dimethyl-benzoic acid. The acid is, therefore, 2,4-dimethyl-benzoyl-*m*-benzoic acid.

One g. of 2,4-dimethyl-benzoyl-*m*-benzoic acid was warmed with thionyl chloride until the reaction ceased and the resulting acid chloride was poured into methyl alcohol. The ester was precipitated by adding water and recrystallized from methyl alcohol, giving small needles; m. p. 73°.

*p*-Carbomethoxy-benzoyl Chloride with *m*-xylene and Aluminum Chloride.—Five g. of *p*-carbomethoxy-benzoyl chloride, 40 cc. of *m*-

<sup>7</sup> Limpriht, *Ann.*, 312, 92 (1900).

<sup>8</sup> Meyer, *Ber.*, 15, 636 (1882).

xylene and 8.5 g. of aluminum chloride were kept at 45° to 50° for 5 hours and then at 80° for 7 hours. The acid product was obtained as in the previous experiment and after recrystallization from methyl alcohol melted at 184° to 5°; yield, 4.5 g.

Silver salt. Calc.  $C_{16}H_{12}O_2Ag$ : Ag, 29.9. Found: 30.0.

Fusion with potassium hydroxide gave benzoic acid, 2,4-dimethylbenzoic acid, and terephthalic acid, identified by the formation of its dimethyl ester. In this case, again, part of the acid decomposed to benzoic acid and 2,4-dimethylbenzoic acid and part to *m*-xylene and terephthalic acid. The acid is, therefore, 2,4-dimethylbenzoyl-*p*-benzoic acid.

The methyl ester of 2,4-dimethylbenzoyl-*p*-benzoic acid prepared from the acid chloride by adding methyl alcohol and recrystallizing from methyl alcohol was obtained as long, colorless needles; m. p. 59°.

### Summary.

1. A method has been described of preparing isophthalic acid and terephthalic acid from commercial xylene.

2. The reaction of each of the carbomethoxy-benzoyl chlorides with aluminum chloride and benzene, toluene, and *m*-xylene, respectively, has been studied. In each case, the reaction with toluene takes place in the *para* position to the methyl group, and with *m*-xylene in the *para* position to one of the methyl groups.

3. New and improved methods of preparing *m*-benzoylbenzoic acid, *p*-benzoylbenzoic acid and some of their derivatives have been given.

4. The following new compounds have been prepared: *p*-toluyl-*m*-benzoic acid, m. p., 172°; methyl-*p*-toluyl-*m*-benzoate, m. p., 108°; 2,4-dimethylbenzoyl-*m*-benzoic acid, m. p. 168°; methyl-2,4-dimethylbenzoyl-*m*-benzoate, m. p. 73°; 2,4-dimethylbenzoyl-*p*-benzoic acid, m. p. 185°; methyl-2,4-dimethylbenzoyl-*p*-benzoate, m. p. 59°.

This research was made under the direction of Professor F. B. Allan.

TORONTO, CANADA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

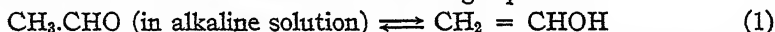
## THE INFLUENCE OF POTASSIUM HYDROXIDE ON THE FORMATION OF VINYL ALCOHOL FROM ACETALDEHYDE.

BY WILLIAM LLOYD EVANS AND CLOYD D. LOOKER.

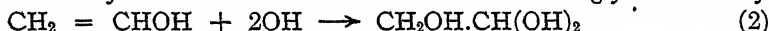
Received May 23, 1921.

When ethyl alcohol<sup>1</sup> and acetaldehyde<sup>2</sup> are oxidized by means of potassium permanganate in the presence of potassium hydroxide, acetic, oxalic and carbonic acids are obtained. The amount of the oxalic acid formed in the oxidation of these organic compounds has been found to be proportional to the concentration of the potassium hydroxide used and also to the temperature employed. In the absence of any added alkali no oxalic acid is formed with either ethyl alcohol or acetaldehyde.

Since acetates are unattacked by solutions of alkaline permanganate under the conditions surrounding these experiments, it was assumed with Nef,<sup>3</sup> Denis,<sup>4</sup> McLeod<sup>5</sup> and others that the intermediate formation of vinyl alcohol was necessary in order to offer a satisfactory explanation for the presence of oxalic acid and carbon dioxide; that is, the acetaldehyde is enolized in accordance with the following equation.



Then the vinyl alcohol so formed would be oxidized to glycollic aldehyde,



which is in turn itself oxidized to oxalic acid and carbon dioxide.<sup>6</sup> A consideration of these facts seems to show that the alkali present in these oxidations must affect the production of vinyl alcohol molecules from acetaldehyde.

Nef<sup>3</sup> found that basic mercuric vinylate  $((\text{CH}_2=\text{CHO})_2\text{Hg}.\text{HgO})$  was formed from an aqueous solution of acetaldehyde and sodium carbonate in the presence of freshly precipitated mercuric oxide. McLeod<sup>5</sup> has observed that no vinyl alcohol is present in an alkaline solution of acetaldehyde if the concentration of the alkali is less than 0.10%; i. e., only acetic acid would be formed by the oxidation of acetaldehyde at alkali concentrations lower than this value. Furthermore, no oxalic acid or carbon dioxide would be formed under these conditions. From the work of Evans and Day<sup>7</sup> and Evans and Adkins<sup>8</sup> it has been shown that the maximum concentration of alkali at which ethyl alcohol and

<sup>1</sup> THIS JOURNAL, 38, 375 (1916); 41, 1267 (1919).

<sup>2</sup> *Ibid.*, 41, 1385 (1919).

<sup>3</sup> Nef, *Ann.*, 298, 315 (1897).

<sup>4</sup> Denis, *Am. Chem. J.*, 38, 568 (1907).

<sup>5</sup> McLeod, *ibid.*, 37, 25 (1907).

<sup>6</sup> THIS JOURNAL, 41, 1280, 1397 (1919).

<sup>7</sup> Evans and Day, *ibid.*, 41, 1282 (1919).

<sup>8</sup> Evans and Adkins, *ibid.*, 41, 1396 (1919).

acetaldehyde are oxidized quantitatively at any given temperature to acetic acid only may be easily calculated.

In view of the above facts, we thought it to be of considerable importance to ascertain the quantitative relationship which might exist between the concentration of the alkali used and the production of vinyl alcohol molecules in an aqueous solution of acetaldehyde.

### Experimental Part.

**Preparation of Acetaldehyde Solution.**—Acetaldehyde was prepared by a modification of the McLeod method<sup>5</sup>. The depolymerized paraldehyde was distilled into a series of small flasks through a 3-bulb Norton and Ott tube, the top bulb of which contained glass beads. The first flask, containing dil. sulfuric acid, was maintained above 40°; the second, between 27° and 40°; the third, between 22° and 27°; the fourth, containing anhydrous cupric sulfate and a calcium chloride tube, below 22°. The cupric sulfate remained almost unchanged in color. The acetaldehyde thus obtained was again distilled below 27° into a weighed amount of water until a sufficient quantity was obtained to make a 2-*M* solution.

**Apparatus and Manipulation.**—The experiment was carried out at 25°. The amount of standardized potassium hydroxide solution chosen

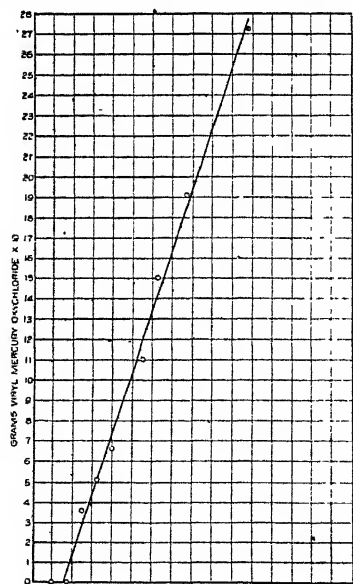


Fig. 1.

for a given experiment was diluted to 145 cc. To the potassium hydroxide solution was added 5 cc. of the acetaldehyde solution (2 *M*) and also 50 cc. of a mercuric chloride solution containing 0.3 g. more of the corrosive sublimate than was necessary to react with the alkali present. The reaction mixture was contained in a 250cc. round-bottom flask and was stirred for 30 minutes. Upon the addition of the mercuric chloride solution the yellow oxide of mercury which formed at first reacted immediately to give a white precipitate with the vinyl alcohol molecules present. This was quickly filtered through an alundum crucible, washed with water, alcohol and ether, then dried over phosphorus pentoxide for 24 hours in a vacuum desiccator. In some experiments the physical

character of the precipitate caused much difficulty in filtration. When the white precipitate was unwashed it changed rapidly into a dark gray

color, this decomposition being accompanied by an evolution of acetaldehyde. After a period of 6 to 8 months, these dark precipitates contained many globules of bright, clean, metallic mercury.<sup>9</sup> However, after being treated as above, the white precipitate remained practically unchanged over a long period of time. The white precipitate obtained in our experiments has remained unchanged in color after two years.

**Character of the Precipitate.**—The white precipitate obtained in these experiments was found to be identical with that obtained by Polleck and Thummel<sup>10</sup> when they attempted to separate mercuric chloride by means of ethyl ether from basic mercuric chloride in potassium or sodium hydrogen carbonate solution. These investigators gave the following formula to their compound,  $\text{CH}_2=\text{CHOHgOHgHgCl}_2$ , and called it vinyl mercury oxychloride. Our analyses showed 82.62% of mercury,<sup>9</sup> (calc. 82.34%).

Nef and Denis<sup>3,4</sup> obtained basic mercury vinylate,  $(\text{CH}_2=\text{CHO})_2\text{Hg}(\text{HgO})$  by a different procedure than that employed in these experiments.

**Results.**—The amounts of vinyl mercury oxychloride formed at the various concentrations of potassium hydroxide used in these experiments are shown in the following table.

KOH per 200 cc. G.	VINYL MERCURY OXYCHLORIDE FORMED.		Acetaldehyde equivalent $\times 10^2$ .
	Molar concentrations of KOH $\times 10^2$ .	$\text{CH}_2=\text{CHOHgOHgHgCl}_2$ . G.	
0.11	0.9804	0.000	0.000
0.20	1.7825	0.003	0.01806
0.28	2.4965	0.36	2.167
0.36	3.2085	0.51	3.071
0.45	4.0107	0.66	3.974
0.62	5.5259	1.10	6.623
0.70	6.2390	1.50	9.031
0.87	7.7540	1.91	11.500
1.20	10.6950	2.72	16.380

From the results of these experiments it is found that the vinyl alcohol production is primarily a function of the concentration of the potassium hydroxide used. Hence it would be expected that the yield of oxalic acid in the oxidation of ethyl alcohol and acetaldehyde by means of potassium permanganate and potassium hydroxide<sup>1,2</sup> would be proportional to the concentration of the alkali used. These results show that a concentration of about 1.40 g. of potassium hydroxide per liter is necessary before an appreciable amount of the white precipitate is obtained. From the experiments of Adkins and one of us<sup>8</sup> it was calculated that a concentration of 1.95 g. of potassium hydroxide per liter is the largest one that may be

<sup>9</sup> Compare *Ber.*, 22, 2867 (1889).

<sup>10</sup> Polleck and Thummel, *ibid.*, 22, 2863 (1889).

employed at 25° without oxalic acid being formed. Hence it is seen that considering the difficulty of handling the white compound of mercury there is a satisfactory concordance in the results of these different experiments.<sup>11</sup> \*

### Summary.

1. Vinyl mercury oxychloride is obtained when alkaline solutions of acetaldehyde are treated with mercuric chloride.

2. The yield of vinyl mercury oxychloride is proportional to the concentration of the alkali present, showing that the production of vinyl alcohol is likewise proportional to the concentration of the alkali.

3. Since the formation of vinyl alcohol is necessary to account for the presence of oxalic acid in the oxidation of ethyl alcohol and acetaldehyde, it follows from (2) that the yield of oxalic acid is also proportional to the concentration of the alkali used.

4. A concentration of about 1.40 g. of potassium hydroxide is necessary for the formation of vinyl at alcohol 25°. This result is in accord with those obtained on the oxidation of acetaldehyde.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY.]

## ADDITION REACTIONS OF PHOSPHORUS HALIDES. IV. THE ACTION OF THE TRICHLORIDE ON SATURATED ALDEHYDES AND KETONES.

By J. B. CONANT, A. D. MACDONALD AND A. MCB. KINNEY.

Received May 28, 1921.

### Introduction.

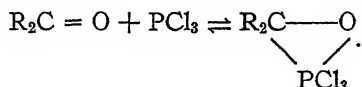
The first paper of this series dealt with the action of phosphorus trichloride on benzaldehyde. The primary addition product formed by these two substances could be decomposed by the action of water or glacial acetic acid with the formation of an  $\alpha$ -hydroxyphosphonic acid. By the use of glacial acetic acid as a medium very good yields of this substance were obtained.<sup>1</sup> The results presented in this paper show that the reaction can be similarly employed for the preparation of hydroxyphosphonic acids from other aldehydes and ketones. The reaction as applied to ketones, however, is of somewhat limited scope. With certain ketones the yields are rather low (about 50%). Aromatic ketones such as benzophenone and benzil, either react only under very much modified conditions, or not at all. Camphor, also, has been found to be very unreactive.

<sup>11</sup> Compare THIS JOURNAL, 41, 1282 (1919); *Am. Chem. J.*, 37, 28 (1907).

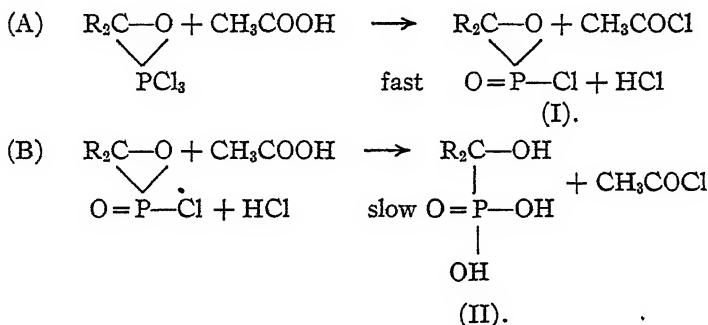
<sup>1</sup> THIS JOURNAL, 42, 2337 (1920).

### The Limits of the Reaction.

The initial reaction between the carbonyl group and the trichloride is reversible. In the case of benzaldehyde,<sup>1</sup> the equilibrium point is such that only about 30% of the material is in combination.



The addition product is more reactive than phosphorus trichloride towards acetic acid or acetic anhydride. Therefore, with these reagents it is possible to cause the reaction to run to completion and, in the case of benzaldehyde, to obtain excellent yields with equimolecular amounts of materials. When the temperature is kept below 30° to 35° the acetic acid reacts so rapidly with the addition product that there is no appreciable reaction with the trichloride.



These equations show the probable course of this reaction; a mixture of both the phosphonic (I) and phosphonic (II) acids (or perhaps their acid chlorides) is actually produced. To obtain the hydroxyphosphonic acid (II), the reaction mixture is always poured into water and heated; this completes the conversion of the phosphonic acid into the hydroxyphosphonic acid, (Reaction B).

In the case of benzophenone, anthraquinone, benzil and camphor no phosphonic acid can be obtained by such a procedure. Obviously, it is not expedient to attempt to accelerate the reaction by raising the temperature; acetic acid and phosphorus trichloride react so rapidly above 30° that no satisfactory results can be obtained even with benzaldehyde. Acetic anhydride is less active and, in certain cases which will be considered in a later paper, it has been possible to obtain results by using this reagent at a temperature of 30° to 35°. It was of no service, however, with the ketones just mentioned.

The failure of the reaction with benzophenone can be attributed to one of three possible causes. (1) The equilibrium of the initial reaction is very

far to the left; (2) the addition product is relatively unreactive with the reagents employed; (3) the rate at which the equilibrium of the initial reaction is attained is very slow. The fact that the materials were recovered quantitatively argues against the second possibility—apparently the initial addition reaction had proceeded to only a very slight extent. An increase in temperature would be expected to accelerate the reaction greatly. By thus making the equilibrium more mobile, it should be possible to approach the conditions which are realized at 25° with simple aldehydes and ketones. The effect of temperature on the equilibrium point cannot be predicted, but the position of the equilibrium is of not much importance *provided the rate of the reaction is relatively great*. In order to parallel the usual procedure at a higher temperature, it is necessary to find some substance to replace the acetic acid. This substance must react only slowly with the trichloride at the given temperature, but rapidly with the addition product. The similarity between the addition product and the pentachloride enabled us to investigate this point by studying the behavior of several reagents towards the pentachloride. A number of experiments with various compounds led us to believe that benzoic acid would be suitable. A trial with this reagent and benzaldehyde at a temperature of 145° to 150° was successful. Benzoyl chloride and the phosphonic acid were formed. The method was then applied to benzophenone with satisfactory results. At a temperature of 155° the reaction seemed to run with benzoic acid much as it did with simple ketones and acetic acid at room temperature; a 50% yield of the desired hydroxyphosphonic acid was obtained. With camphor there was also apparently a reaction, although the product was not isolated in a pure state. Anthraquinone and benzil could not be made to react even by this procedure, and it has not been possible, as yet, to cause them to combine with phosphorus trichloride.

### Isolation of the Product.

The isolation of the hydroxyphosphonic acid is a difficult problem in many cases. Many of the substances crystallize with difficulty and are very soluble in water. Evaporation of the aqueous solution in some instances yields a gum which slowly solidifies. After drying on a porous plate it can be recrystallized. In some cases no crystalline acid could be obtained and the product was isolated as the lead salt.

The reaction with acetophenone and acetone is complicated by the fact that an unsaturated phosphonic acid is also formed to some extent. This was first noticed because the aqueous solution of the product rapidly decolorizes bromine water. In this work the weight of the crude mixture of saturated and unsaturated acids was determined and the yield calculated from this. A subsequent paper will discuss the mechanism of the



formation of these acids which have the formula  $RC(PO_3H_2)=CH_2$ . The unsaturated acid was obtained pure in the case of acetophenone. Its structure follows from its oxidation to formaldehyde by chromic acid.

The results of this research indicate the limits of the reaction of the trichloride with unsubstituted aldehydes and ketones. The results are summarized in the following table. An excess of trichloride was used in every case. As this varied with the experiment and the conditions of isolating the material are obviously inaccurate, the variations in the yields are of no great significance.

Carbonyl compound.	Medium.	Yield of phosphonic acid. %	How isolated.
$C_6H_5COCH_3$	$CH_3COOH$	96	crude mixture, partially unsaturated.
$CH_3COCH_3$	$CH_3COOH$	91	crude mixture, partially unsaturated.
$CH_3COCH_2CH_3$	$CH_3COOH$	76	as lead salt.
$C_2H_5COC_2H_5$	$CH_3COOH$	67	as lead salt.
$(CH_3)_3CCOCH_3$	$(CH_3CO)_2O$	56	as lead salt.
$CH_3(CH_2)_5CHO$	$CH_3COOH$	76	as lead salt.
$(C_6H_5CH_2)_2CO$	$CH_3COOH$	44	crude crystals.
$C_6H_5CH_2CH_2COC_6H_5$	$CH_3COOH$	48	recrystallized acid.
$(C_6H_5CH_2CH_2)_2CO$	$(CH_3CO)_2O$	56	recrystallized acid.
$C_6H_5COC_6H_5$	$C_6H_5COOH$ (150°)	50	recrystallized acid.
Camphor	$C_6H_5COOH$ (150°)		not isolated.
$C_6H_5COCOC_6H_5$			no reaction under any conditions.
Anthraquinone			no reaction under any conditions.

### Experimental.

#### General Procedure with Acetic Acid.

The general procedure which was employed when acetic acid was used as a medium is essentially as follows. The phosphorus trichloride was added to the carbonyl compound, while the temperature was kept below 35°; this requires considerable cooling in some cases. An excess of the trichloride was employed; this was usually only about 10%, but in certain cases was much more. The mixture was protected from moisture and allowed to stand for from 2 to 3 hours. A slight excess (three times the molecular amount) of glacial acetic acid was then added, while the temperature was kept between 20° and 30°. After the reaction mixture had stood 12 hours longer, it was poured into 300 cc. of ice-water and shaken vigorously. The aqueous solution was now evaporated to dryness on the steam-bath. The gum which formed was allowed to crystallize. In some cases this was a very slow process and took from one day to two weeks. The crystalline mass could then be dried on a clay plate and finally in a vacuum desiccator over sodium hydroxide.

In those cases in which no crystallization took place, the lead salt was prepared. The gum was dissolved in about 200 cc. of water, made strongly alkaline with ammonia and then treated with magnesium nitrate. After

it had stood overnight, the precipitated magnesium ammonium phosphate was filtered off. The solution was then diluted to 500 cc., made just acid with acetic acid, and heated to boiling. A solution of lead acetate or nitrate was added in excess, the mixture was boiled for 5 or 10 minutes to coagulate the lead salt and the solution was filtered. The lead salt was washed with boiling water and then dried. Prepared in this way, the lead salt was free from phosphate and practically free from chloride. Experiments had shown that the phosphorous acid, first formed by the excess of the trichloride and the water, would be completely oxidized to phosphoric acid during the evaporation. Thus, there was no necessity of removing this acid from the mixture. Most of the hydrochloric acid also is removed during the evaporation; the amount that is left does not interfere, since lead chloride is soluble in boiling solution whereas the lead salts of the phosphonic acids are practically insoluble.

**Acetophenone.**—Ten g. of acetophenone and 15 g. of trichloride (25% excess) yielded 16 g. of crude acid after it had been dried for 15 hours. The crude material contained about 63% of the unsaturated acid. The theoretical yield of the hydroxy acid would be 16.7 g. Percentage yield, about 96%. The pure unsaturated acid may be obtained by crystallization from a mixture of benzene and carbon tetrachloride.

**$\alpha$ -Phenyl-vinyl-phosphonic Acid,  $C_6H_5C(PO_3H_2)=CH_2$ .**—The acid, thus prepared, is very soluble in water, fairly soluble in alcohol and only slightly soluble in benzene. It melts at  $112^\circ$ .

**Analyses.** Calc. for  $C_8H_9O_3P$ : P, 16.9; C, 52.2; H, 4.9. Found: P, 16.6; C, 52.2; H, 5.2.

The acid was shown to be dibasic by titration with standard alkali. The aniline salt was made by the action of aniline on an alcohol-ether solution of the acid. It was recrystallized from alcohol and melted at  $180^\circ$  to  $181^\circ$ . It was soluble in water and insoluble in ether.

**Analysis.** Calc. for  $C_{14}H_{16}O_3NP$ : N, 5.15. Found: 5.09.

The phenyl-vinyl-phosphonic acid decolorizes bromine water immediately and bleaches permanganate solution. Its structure follows from these reactions, its analysis and the formation of formaldehyde on oxidation with chromic acid. 0.1 g. of substance was oxidized with 0.2 g. of chromic acid and the evolved gases passed into water. The water gave the characteristic resorcin test for formaldehyde.

**Acetone.**—Ten g. of acetone and 30 g. of trichloride (12% excess) yielded a crystalline mass which, when dry, weighed 17 g. A sample titrated with bromine water showed that it contained about 30% of an unsaturated acid. By recrystallization from hot glacial acetic acid, the  $\alpha$ -hydroxy-*isopropyl*-phosphonic acid was obtained, m. p.  $167^\circ$  to  $169^\circ$ . The same acid has been prepared by Marie<sup>2</sup> by adding phosphorous acid to acetone and oxidizing the product. The percentage yield, based on the weight of the crude material was 91%.

**Methylethyl Ketone.**—Ten g. of methylethyl ketone and 25 g. of trichloride (30% excess) yielded 38 g. of the lead salt, or 76% calculated amount. No crystalline acid could be obtained.

**Lead Salt of  $\alpha$ -hydroxy- $\alpha$ -methyl-propyl-phosphonic Acid,  $C_2H_5C(PO_3Pb)OHCH_3$ .**—The salt is insoluble in hot and cold water, but soluble in fairly strong nitric acid. It

<sup>2</sup> Marie, *Compt. rend.*, 133, 221 (1901).

was free from phosphates and chlorides. A sample of it, when tested with bromine water, showed that it contained only a trace of unsaturated acid.

*Analysis.* Calc. for  $C_4H_9O_4PPb$ : Pb, 55.7. Found: 55.5.

**Ethylpropyl Ketone.**—Ten g. of ethylpropyl ketone and 15 g. of trichloride (7% excess) yielded 25.8 g. of lead salt, (67%). No crystalline acid could be obtained; a thick oil only partially soluble in water but soluble in alkalis could be isolated but not purified.

**Lead Salt of  $\alpha$ -Hydroxy- $\alpha$ -ethyl-butyl-phosphonic Acid,  $C_4H_7C(PO_3Pb)OHC_2H_5$ .**—The salt was free from chlorides and contained only a trace of unsaturated acid.

*Analysis.* Calc. for  $C_6H_{13}PO_4Pb$ : Pb, 53.5. Found: 54.4.

**Pinacolone.**—Acetic anhydride was substituted for the acetic acid in the experiments with this compound. The resulting phosphonic acid is very unstable and there seemed to be less decomposition with acetic anhydride as a medium than with acetic acid. During the mixing of the ketone and the trichloride the temperature must be kept below 25°. After the addition of the anhydride the temperature was kept at 30° to 35° for several hours, then the mixture was poured into water. A dark oil separated from the aqueous solution. The acid was unstable, particularly when warmed, and could not be obtained crystalline. A lead salt was prepared by the usual procedure. 10 g. of pinacolone and 15 g. of trichloride (17% excess) gave 22.6 g. of lead salt, a 56% yield.

**Lead Salt of  $\alpha$ -hydroxy- $\alpha$ -methyl- $\beta$ -dimethyl-propyl-phosphonic Acid,  $(CH_3)_3C-C(PO_3Pb)(OH)(CH_3)$ .** The salt was very hygroscopic. After drying it for a month in a vacuum desiccator over sulfuric acid it gave the following analysis.

Calc. for  $C_6H_{13}O_4PPb$ : Pb, 52.6. Found: 51.4, 51.4.

The low values may be due to water still in combination with the compound. The salt was free from phosphate, chloride and unsaturated compounds.

**Heptyl Aldehyde.**—Ten g. of *n*-heptyl aldehyde and 16 g. (25% excess) of trichloride gave 12 g. of a lead salt or a yield of 76%. The gum obtained by evaporation of the aqueous solution of the reaction mixture slowly solidified; it was converted into the lead salt in order to determine the yield. When the lead salt was decomposed with hydrogen sulfide and the aqueous solution evaporated, the crystalline acid could be obtained.

In another experiment in which a somewhat purer sample of aldehyde was used in slight excess, 11 g. of solid phosphonic acid was obtained (76%) yield. Recrystallization from water yielded the pure hydroxyphosphonic acid melting at 165° to 173°. The compound is identical in its properties with the hydroxyphosphonic acid made by Fossick from an excess of trichloride and heptylaldehyde.<sup>3</sup>

**Dibenzyl Ketone.**—Five g. of the ketone and 6 g. of the trichloride (90% excess) yielded a crystalline mass which weighed 3 g. when dry. A test showed that no unsaturated acid was present.

**$\alpha$ -Benzyl- $\alpha$ -hydroxy- $\beta$ -phenyl-ethyl-phosphonic Acid,  $C_6H_5CH_2(PO_3H_2)OHCH_2C_6H_5$ .**—The acid can be recrystallized from benzene. It melts at 181° to 182°.

*Analysis.* Calc. for  $C_{18}H_{17}O_4P$ : C, 61.4; H, 5.8; P, 10.6. Found: C, 61.3; H, 5.9; P, 10.6.

**Benzyl-acetophenone.**—Three g. of the ketone and 3 g. of trichloride (20% excess) yielded 5 g. of sticky crystals. These were dissolved in glacial acetic acid, and water was added very slowly to the solution kept at -10°. The crystals which formed could be recrystallized from benzene. Two g. of purified acid was obtained, a 48% yield.

**$\alpha$ -Phenyl- $\alpha$ -hydroxy- $\gamma$ -phenol-propyl-phosphonic Acid,  $C_6H_5C(PO_3H_2)OHCH_2CH_2$**

<sup>3</sup> Fossick, *Monatsh.*, 7, 27 (1886).

$C_6H_5$ .—The acid melts at  $165^\circ$  to  $168^\circ$ ; it is practically insoluble in water, but is soluble in alcohol, ether and acetic acid. It did not decolorize bromine water.

*Analysis.* Calc. for  $C_{15}H_{16}PO_4$ : P, 10.6. Found: 10.8.

**Dibenzyl-acetone.**—Two g. of the ketone and 2 g. of the trichloride (80% excess) yielded 5 g. of very impure crystals which, however, contained no unsaturated acid. Recrystallization from benzene yielded 1.5 g. of pure solid (56%). Acetic anhydride was used as the medium in this experiment.

**$\alpha$ -hydroxy- $\alpha$ -( $\beta$ -phenyl ethyl)- $\gamma$ -phenyl-propyl-phosphonic Acid,  $(C_6H_5CH_2CH_2)_2C(OH)(PO_3H_2)$ .**—This substance melts at  $173^\circ$  to  $174^\circ$ . It is insoluble in water but completely soluble in a solution of sodium hydrogen carbonate.

*Analysis.* Calc. for  $C_{17}H_{21}O_4P$ : P, 9.7. Found: 10.6.

### Procedure with Benzoic Acid at a High Temperature.

As stated in the introduction, benzil, camphor, benzophenone and anthraquinone were recovered completely unchanged by all procedures involving acetic acid or anhydride. Not a trace of a phosphonic acid could be detected. The high temperature procedure in which benzoic acid is used was first tried with benzaldehyde as described in the following experiment.

Ten g. of benzaldehyde and 40 g. of benzoic acid were mixed in a flask equipped with a reflux condenser, and heated on the steam-bath. Sixteen g. of phosphorus trichloride (1.3 mols) was added and the reaction mixture heated to  $150^\circ$ . After 45 minutes the molten mass was poured into 300 cc. of water and the mixture was heated on the steam-bath until all the material had dissolved. The solution was then cooled in ice and the benzoic acid filtered off. The filtrate was evaporated to dryness, the residue dissolved in 10 cc. of water and a small amount of benzoic acid filtered off. The filtrate was evaporated to dryness and the phosphonic acid converted into the aniline salt by treatment with aniline in an alcohol-ether solution. Several crystallizations of the aniline salt from alcohol yielded 7.4 g. of material melting at  $201^\circ$ . It was identical with the aniline salt previously described.<sup>1</sup> The yield of purified material was 26% of that calculated.

**Benzophenone.**—Ten g. of benzophenone and 20 g. of benzoic acid were mixed and heated on the steam-bath until molten. Ten g. of phosphorus trichloride (55% of excess) was added in small portions during a period of 5 to 10 minutes. The temperature was gradually raised in the course of 10 minutes to  $155^\circ$ , and then allowed to fall to  $130^\circ$  and kept constant at this point for 2 to 3 hours. The melt was cooled to  $90^\circ$  and poured into 500 cc. of water. The mixture was made strongly alkaline with sodium hydroxide and heated on the steam-bath for from 4 to 5 hours. During this treatment, the oil which separated when the melt was first poured into water, decreased appreciably. The solution was diluted to 750 cc., cooled and the unchanged benzophenone removed by extracting it with ether. To separate the benzoic acid, the solution was acidified strongly with hydrochloric acid, then cooled and filtered. The filtrate was evaporated to a volume of 250 cc. and extracted thrice with ether. The ethereal solution on evaporating yielded an oil which finally solidified. Fractional crystallization from slightly acidulated water gave 7 g. of a phosphonic acid melting at  $171^\circ$  to  $172^\circ$ , and 2.5 g. of another acid containing phosphorus whose constitution was not established. Perhaps it was formed by the replacement of a hydrogen atom of the nucleus by the radical  $-PCl_2$ .

**$\alpha$ -Hydroxy-diphenyl-methyl-phosphonic Acid**,  $(C_6H_5)_2C(OH)(PO_3H_2)$ .—The acid melts at  $171^\circ$  to  $172^\circ$ . It is readily soluble in alcohol, in ether and in hot water and somewhat soluble in cold water.

*Analysis.* Calc. for  $C_{13}H_{13}O_4P$ : P, 11.7. Found: 11.7.

The constitution of the acid is established by the fact that it is oxidized by permanganate with the formation of benzophenone and phosphonic acid. Two g. of the acid dissolved in 10 cc. of sodium carbonate solution was treated with potassium permanganate until a permanent pink color resulted. The dioxide and a yellow solid separated and were filtered off. The filtrate gave a strong test for the phosphate ion. The yellow solid on recrystallization gave 0.5 g. of benzophenone which was identified by the method of mixed melting points.

**Camphor.**—The procedure just outlined for benzophenone was applied to camphor. A few grams of an oil was obtained, evidently an acid material, slightly soluble in water and containing phosphorus. No large amount of crystalline material could be secured, so the compound was not investigated further.

Anthraquinone and benzil showed no evidence of reaction when treated by the high temperature-benzoic acid procedure. The materials were recovered unchanged and no trace of a phosphonic acid could be detected.

### Summary.

1. The limits of the action of phosphorus trichloride on saturated aldehydes and ketones has been studied. By the use of glacial acetic acid or acetic anhydride as a medium, hydroxyphosphonic acid can be obtained from most ketones.

2. The products were isolated either as crystalline acids or as lead salts.

3. With acetophenone and acetone, an unsaturated phosphonic acid is also produced. This has been isolated in one instance and its constitution established.

4. Benzophenone will not combine with phosphorus trichloride by the usual procedure. At  $150^\circ$ , with benzoic acid in place of acetic acid satisfactory results can be obtained.

5. It has not been possible by any procedure to add the trichloride to benzil or anthraquinone.

[CONTRIBUTION FROM THE UNIVERSITY OF MANCHESTER.]

THE PREPARATION OF PYRIDINE AND OF CERTAIN OF ITS  
HOMOLOGS IN A STATE OF PURITY.

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Received June 8, 1921.

The preparation of highly purified pyridine has not yet been described, while in the case of its homologs widely discordant results are recorded for the physical properties. It was therefore considered of interest to undertake the preparation of the bases in a pure form.

## Pyridine.

Crude coal tar bases vary greatly both in the nature and in the proportion of the bases which they contain. The nature of the bases depends on whether they are derived from light or middle oil. The following results were obtained with bases derived from a light oil.

The crude bases were dehydrated with solid sodium hydroxide. From 2 liters 800 cc. of a pyridine fraction, b. p.  $113^{\circ}$  to  $117^{\circ}$ , and 200 cc. of a 2-methylpyridine fraction, b. p.  $127^{\circ}$  to  $130^{\circ}$ , were obtained after six successive fractional distillations through a glass fractionating column 110 cm. long and 2 cm. in diameter (Col. A).

Pure pyridine was obtained by converting the former fraction into the pure compound  $2C_5H_5N \cdot ZnCl_2$ . For this purpose, 845 g. of zinc chloride is dissolved in a mixture of 690 cc. of water, 345 cc. of conc. hydrochloric acid (sp. gr. 1.18) and 690 cc. of absolute alcohol. One liter of the pyridine fraction is added to this mixture.

A crystalline precipitate is obtained which is separated from the mother liquor and recrystallized twice from absolute alcohol. To liberate the base, a concentrated aqueous solution of 26.7 g. of sodium hydroxide is added to 100 g. of the dry recrystallized compound. The base with dissolved water is separated from the precipitate by filtration and is dried over solid sodium hydroxide. This sample of pyridine, on distillation in a dry apparatus, distills completely at  $115.3^{\circ}$ , measured on the international hydrogen scale, under 760 mm. of mercury. The mass of 1 cc. of pyridine at  $25^{\circ}$  ( $d_4^{25}$ ) is 0.9776 g. All weighings were corrected for air displacement. Previous determinations of the boiling point are as follows.

Innes,<sup>1</sup>  $115.2^{\circ}$  to  $115.5^{\circ}$ ; Constam and White,<sup>2</sup>  $115.2^{\circ}$ ; Zawidzki,<sup>3</sup>  $115.1^{\circ}$  to  $115.3^{\circ}$ ; Hartley, Thomas and Applebey,<sup>4</sup>  $115.3^{\circ}$  to  $115.4^{\circ}$ . The density ( $d_4^{25}$ ) is variously given as 0.97721 (Hartley, Thomas and Applebey), 0.97795 (Zawidzki), 0.97832 (Dunstan, Thole and Hunt).<sup>5</sup>

<sup>1</sup> Innes, *J. Chem. Soc.*, 79, 261 (1901).

<sup>2</sup> Constam and White, *Am. Chem. J.*, 29, 1 (1903).

<sup>3</sup> Zawidzki, *Chem. Ztg.*, 30, 299 (1906).

<sup>4</sup> Hartley, Thomas and Applebey, *J. Chem. Soc.*, 93, 538 (1908).

<sup>5</sup> Dunstan, Thole and Hunt, *ibid.*, 91, 1738 (1907).

## 2-Methylpyridine.

2-methylpyridine can be prepared by a method analogous to the method for 3-methylpyridine, if the fraction distilled from crude bases between 127° and 130° is used. The resulting product, in a dry apparatus, distils completely at 127.8° to 9°, measured on the international hydrogen scale, under 760 mm. of mercury. The mass of 1 cc. at 25° ( $d_{4}^{25}$ ) is 0.9404 g. when all weighings are corrected for air displacement.

Thorpe<sup>6</sup> gives b. p. 133.5°;  $d_{4}^{25}$  0.9384,  $d_{4}^{20}$  0.9616; Ladenburg and Lange<sup>7</sup> give b. p. 129°,  $d_{4}^{20}$  0.9652; Constam and White<sup>2</sup> give b. p. 128.8,  $d_{4}^{15}$  0.9497; Garrett and Smythe<sup>8</sup> give b. p. 129.4°.

## 3-Methylpyridine.

(A) Two liters of crude bases derived from a light oil was dehydrated with solid sodium hydroxide and the dry oil was fractionally distilled twelve times successively through a Young's<sup>9</sup> 8-chamber evaporator fractionating column, 110 cm. long and 3 cm. in diameter. Fractions were collected at every degree from 120° to 150°. The fraction 143° to 144° (227 cc.) was converted into the zinc chloride compound,  $2C_6H_7N \cdot ZnCl_2$ , by dissolving it in 1135 cc. of water and adding the solution to a conc. aqueous solution of 243 g. of zinc chloride clarified by treatment with hydrochloric acid. The precipitate was separated from the mother liquor, dried, and weighed. The 360 g. obtained was dissolved in 1400 cc. of boiling absolute alcohol. When the solution was cooled to room temperature, the zinc chloride compound crystallized. It was recrystallized from alcohol, until its melting point, determined in a sealed tube, was unaltered by further crystallization. Four crystallizations sufficed, and the melting point was 115°. The 93 g. of the zinc chloride compound of 3-methylpyridine obtained, was decomposed by treatment with a concentrated aqueous solution of 24 g. of sodium hydroxide. The base containing dissolved water, separated by filtration, was dried over solid sodium hydroxide. When placed in a dry apparatus, it distilled completely at 143.8°, measured on the international hydrogen scale, under 760 mm. pressure. The mass of 1 cc. at 25° is 0.9515 g. All weighings were corrected for air displacement.

Previous determinations of the boiling point are as follows: Schwarz,<sup>10</sup> 143.5°; Constam and White,<sup>2</sup> 143.4°; Flaschner,<sup>11</sup> 143.9°; Constam and White give  $d_{4}^{15}$  0.96134 for 3-methylpyridine.

The base obtained in this manner was found to be completely miscible with water between 15° and 100°. It was identified as 3-methylpyridine by oxidation to the

<sup>6</sup> Thorpe, *J. Chem. Soc.*, 37, 222 (1880).

<sup>7</sup> Ladenburg and Lange, *Ann.*, 247, 6 (1888).

<sup>8</sup> Garrett and Smythe, *J. Chem. Soc.*, 81, 452 (1902).

<sup>9</sup> "Fractional Distillation," The Macmillan Company, 1903.

<sup>10</sup> Schwartz, *Ber.*, 24, 1676 (1891).

<sup>11</sup> Flaschner, *J. Chem. Soc.*, 95, 668 (1909).

carboxylic acid, pyridine-3-carboxylic acid, which without further purification melted sharply at  $228^{\circ}$  in a sealed tube. Since the acid gave no red coloration with ferrous sulfate solution, complete absence of any 2-6 dimethylpyridine in the sample of 3-methylpyridine may be assumed.

The oxidation was carried out in the following manner. Four g. of the base was dissolved in 400 cc. of water and 13.6 g. of potassium permanganate added. The mixture was heated on the steam-bath and a continuous stream of carbon dioxide ~~was~~ passed through it during the period of oxidation. The passage of carbon dioxide improves the yield of the carboxylic acid, presumably because the free potassium hydroxide formed during oxidation in the absence of carbon dioxide, decomposes the acid with formation of pyridine.

After 6 hours, the hot liquid was filtered. The precipitate of manganese dioxide was boiled with water and the solution filtered. The combined filtrates were concentrated to small volume, neutralized with sulfuric acid, cooled and treated with silver nitrate. The solid silver salt of pyridine-3-carboxylic acid was collected on a filter and washed with distilled water; then it was suspended in distilled water and a stream of hydrogen sulfide was passed through the liquid. After the liquid had been boiled, the precipitate of silver sulfide was removed and the filtrate was evaporated to dryness. A white residue of the carboxylic acid was obtained; m. p.  $228^{\circ}$ .

(B) 3-Methylpyridine can also be obtained from crude pyridine bases of middle oil. The crude bases were dried over solid sodium hydroxide and 3 liters of the dry oil was 5 times successively fractionally distilled through Column A; fractions were collected every degree from  $139^{\circ}$  to  $170^{\circ}$ . The fractions from  $139^{\circ}$  to  $143^{\circ}$ , total volume 200 cc., were combined and converted into the zinc chloride compound by the method described under (A). An oil separated which would not crystallize even on standing for 24 hours. This oil was collected, dissolved in 800 cc. of boiling alcohol and concentrated to half the volume. Crystallization could be brought about only by cooling the solution to  $-15^{\circ}$ . (The further treatment of the mother liquor is described under the preparation of 2,6-dimethylpyridine.) The crystals were redissolved in 250 cc. of boiling alcohol and the solution was cooled again to  $-15^{\circ}$ . The crystals which then separated were dissolved once more in 250 cc. of boiling alcohol. When this solution cooled to room temperature, crystallization occurred. Two recrystallizations from 250 cc. of alcohol sufficed to give a product, m. p.  $115^{\circ}$ , whose melting point was unaltered on recrystallization.

The base obtained from these crystals was identical in all respects with the 3-methylpyridine described under (A).

We find that 3-methylpyridine is completely miscible in all proportions with water between 15 and  $100^{\circ}$ ; therefore our results conflict with those of Flaschner<sup>11</sup> who states that 3-methylpyridine is only partially miscible with water. There is no doubt that Flaschner was dealing with a mixture containing 2,6-dimethylpyridine, which we find to be partially miscible with water, and that he did not obtain pure 3-methylpyridine. In contrast to our procedure, Flaschner did not identify any of the materials/



he dealt with. Therefore we can state positively that his re 3-methylpyridine are incorrect.

It is difficult to see how Flaschner could have obtained 4-pyridine by crystallization of the zinc chloride compound, since C and White<sup>2</sup> state that 4-methylpyridine is a very weak base. Bo-stam and White, and Meisenheimer<sup>12</sup> had to resort to crystallization mercuric chloride compound for the preparation of this base. In ad we have failed entirely to repeat Flaschner's preparation of 4-methylpyridine, the product which we obtained proving to be 3-methylpyridine.

### 2,6-Dimethylpyridine.

When the alcoholic mother liquor from the first crystallization of zinc chloride compound of 3-methylpyridine (Section B under "3-methylpyridine") stood for several days, it separated into two layers. The sirupy layer contained the whole of the zinc chloride compound and separated (224 g.). Fifty g. of sodium hydroxide was added in the of a concentrated aqueous solution and the regenerated base dried sodium hydroxide. The 107 cc. of base obtained was mixed with 10% of conc. hydrochloric acid (sp. gr. 1.18) and then added to a solution 542 g. of mercuric chloride dissolved in 2 liters of boiling alcohol. The compound,  $C_7H_9N.HCl.2HgCl_2$ , which separated when the solution was cooled to 15° was recrystallized five times from 1400 cc. of boiling alcohol. The product obtained melted at 131° in a sealed tube, and its melting point was unaltered by further crystallization. Yield, 147 g. This was decomposed with a concentrated aqueous solution of 50 g. of sodium hydroxide. The base containing dissolved water separated by filtration from the precipitated mercuric oxide was dried over solid sodium hydroxide and distilled in a dry apparatus. Thus only 13 g. of pure base was obtained and in consequence an accurate reading of the boiling point was not possible; that observed was about 137.5°. The mass of 1 cc. of 2,6-dimethylpyridine at 25° is 0.9200 g. The base was not completely miscible with water at 90°. It was identified as 2,6-dimethylpyridine by oxidation to pyridine-2,6-dicarboxylic acid, which melted sharply at 228° in a sealed tube. In an open tube the acid melted with decomposition. An aqueous solution of the acid, on addition of ferrous sulfate solution, gave a red color, followed by precipitation of a grayish precipitate, presumably an iron salt of the acid. The red coloration indicates the presence of a methyl group in Position 2 in the original base.

### 2,4-Dimethylpyridine.

The material used for the preparation of this base was the fractions distilled between 155° and 156°, and between 156° and 157°, obtained in the

<sup>12</sup> Meisenheimer, *Ann.*, 420, 197 (1920).

ation described under "3-Methylpyridine," Section B. The total 200 cc., was converted into the compound  $C_7H_9N.HCl.2HgCl_2$  by adding it with 187 cc. of conc. hydrochloric acid and adding the mixture to a solution of 950 g. of mercuric chloride in 3600 cc. of boiling absolute alcohol. The compound which separated as the solution cooled to  $15^\circ$  was crystallized four times from 1 liter of boiling alcohol. The melting point of the product was  $128^\circ$ , which remained unaltered by further recrystallization. The yield was 80 g.

The base was regenerated by treatment with a concentrated solution of 19 g. of sodium hydroxide. The base containing dissolved water was separated from the precipitate by filtration and was dried over solid calcium hydroxide. Through a dry apparatus the base distilled completely at  $1^\circ$  under 760 mm. pressure. The mass of 1 cc. at  $25^\circ$  is 0.9273 g.

In water it gives a minimum critical solution temperature of  $22.5^\circ$ . The base was identified as 2,4-dimethylpyridine by oxidation to pyridine-2,4-dicarboxylic acid by the method described in the case of 3-methylpyridine, using double the proportion of potassium permanganate. The product melted sharply at  $241^\circ$ ; vigorous evolution of carbon dioxide commenced at once, indicating a dicarboxylic acid. An aqueous solution of the acid gave a deep red coloration with ferrous sulfate solution, which indicates a methyl group in Position 2 in the original base.

### Summary.

Pure samples of pyridine and certain of its homologs have been prepared. Boiling points and densities have been determined and found to be as follows: pyridine, b. p.  $115.3^\circ$ ,  $d_4^{25}$  0.9776; 2-methylpyridine, b. p.  $128-9^\circ$ ,  $d_4^{25}$  0.9404; 3-methylpyridine, b. p.  $143.8^\circ$ ,  $d_4^{25}$  0.9515; 2,6-dimethylpyridine, b. p. about  $137.5^\circ$ ,  $d_4^{25}$  0.9200; 2,4-dimethylpyridine, b. p.  $157.1^\circ$ ,  $d_4^{25}$  0.9273.

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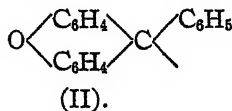
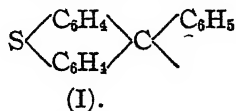
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

### PHENYL-THIO-XANTHYL.

BY M. GOMBERG AND WESLEY MINNIS.

Received June 8, 1921.

The free radical, phenyl-thio-xanthyl (I), differs structurally from phenyl-xanthyl (II) only in the substitution of a sulfur for an oxygen



atom. The difference in the degree of dissociation of the dimolecular ~~two~~ radicals, as reported in the literature, is therefore





quite perplexing. Schlenk and Renning<sup>1</sup> found 82% of the latter substance to be monomolecular by determining the molecular weight in a boiling benzene solution of 1.5% concentration, while they report only 14% of the former to be monomolecular in freezing benzene (0.7% solution). A later investigation<sup>2</sup> showed phenyl-xanthyl to be 70% monomolecular in freezing naphthalene (1.5% solution).

As Schmidlin<sup>3</sup> justly observes, molecular-weight determinations of free radicals are of value only when accompanied by the determinations of oxygen absorption. Otherwise unnoticed transformations or isomerizations of the radicals may vitiate the results. The results of Gomberg and Schoepfle on phenyl-xanthyl were checked by parallel oxygen absorptions; it now seemed desirable to repeat the investigation of phenyl-thio-xanthyl, controlling the work by this essential test.

Phenyl-thio-xanthenol chloride,  $\text{S} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_5 \\ \diagdown \text{Cl} \end{array}$  —Phenyl-thio-

xanthenol was prepared from thio-xanthone and phenyl magnesium bromide,<sup>4</sup> the thio-xanthone having been made from thiosalicylic acid.<sup>5</sup> The xanthenol used in this work was recrystallized from hot petroleum ether (100–110°), and had a melting point of 105° or over.

The red additive compound, phenyl-quino-thio-xanthenol chloride-hydrochloride<sup>6</sup> was made by passing a slow stream of dry hydrogen chloride into a concentrated ethereal solution of the carbinol. It is quite insoluble in this solvent. The red crystals were quickly filtered, washed, and dried in a vacuum desiccator over sulfuric acid.

Various procedures were investigated in order to arrive at the most satisfactory method for removing the extra molecule of hydrochloric acid. The simplest procedure proved to be the best. Ten g. of chloride-hydrochloride was suspended in 100 cc. of dry benzene in a distilling flask which carried an extra side arm sealed into the bulb. Through a glass tube inserted in this side arm there bubbled through the liquid a stream of air, dried by passing through conc. sulfuric acid and phosphorus pentoxide. The flask was heated in a glycerine bath to 90°, the solid gradually went into solution and the deep red color lightened considerably. The solvent was completely distilled in the course of 1½ hours, the last portion being removed under reduced pressure to avoid superheating. On cooling, the deep red oil became a mass of lighter colored crystals, from which after recrystallization from a large quantity of dry ether in the absence of moist air, colorless crystals of chloride were obtained. They turned reddish when dried in a stream of air, in spite of most efficient drying systems. Once dry, the crystals could be preserved in a vacuum desiccator for a long time with little change. Yield 60 to 70%.

*Analysis.* Calc. for  $\text{C}_{18}\text{H}_{13}\text{ClS}$ : Cl, 11.50. Found: 11.30.

<sup>1</sup> Schlenk and Renning, *Ann.*, 394, 188 (1912).

<sup>2</sup> Gomberg and Schoepfle, *This Journal*, 39, 1671 (1917).

<sup>3</sup> Schmidlin, "Das Triphenylmethyl," 1914, p. 159.

<sup>4</sup> Gomberg and Cone, *Ann.*, 376, 201 (1910).

<sup>5</sup> Davis and Smiles, *J. Chem. Soc.*, 97, 1296 (1910).

<sup>6</sup> Gomberg and Cone, *Ann.*, 376, 202 (1910).

In this preparation, heating for too long a period gives a deep red gum which will not crystallize, or else crystallizes as an impure product, and in lower yield.

**Oxygen Absorptions.**—The preparation of the free radical is difficult because of the sensitivity of the chloride to traces of water, with which it forms carbinol and hydrochloric acid, retaining the latter as the additive salt. The presence of free acid has been shown repeatedly to be harmful to the existence of a free radical. The instability of this free radical, as indicated by the following data, may be due to the influence of acid, although it is also possible that the radical spontaneously polymerizes because of other influences, *e. g.*, light, heat. The nature of the solvent is clearly an important factor, so far as the speed of the change is concerned.

All measurements were made by sealing chloride, molecular silver, and the solvent in a glass tube, shaking at room temperature for the specified time, and measuring the absorption of oxygen in the usual apparatus.<sup>7</sup>

Wt. of Chloride. G.	Time of Shaking.	Oxygen Absorbed.	
	Hours. Using Bromobenzene as solvent.	Cc. (N. T. P.)	% of Calc.
0.5630	0.5	21.3	104.4
0.4536	0.5	18.0	109.1
0.7535	1.0	27.2	99.3
0.6840	5.25	25.3	102.0
0.6080	18.0	19.5	88.2
0.5953	41.0	14.6	67.6
0.3971	<i>a</i>	14.0	97.2
	Using Benzene as solvent.		
0.8600	0.5	29.8	95.5
0.5800	0.5	20.2	95.7
0.5399	0.5	15.5	79.1
0.5480	0.5	15.5	77.9
0.5725	0.5	17.1	82.2
0.8425	0.5	25.9	84.6
0.7976	1.0	23.5	81.0
0.8940	3.0	24.7	76.0
0.8200	3.0	18.5	62.1
0.4848	6.0	7.5	42.6
0.4777	14.5	4.6	26.6

(*a*) Shaken with solvent and silver in absorption apparatus.

This record of the progressive disappearance of the free radical in solution, as time elapses, makes its instability most apparent and indicates the improbability of isolating it in the solid state.

**Attempts to Isolate the Free Radical.**—Preliminary trials with chloride and silver, shaken in ether, acetone or ethyl acetate, showed the latter two to be undesirable, since the brown-red solutions changed to a straw yellow in 24 hours. The free radical in solution possesses high tinctorial power; no difference in shade or depth of color can be noted between benzene or bromobenzene solutions giving either high or low values for

<sup>7</sup> Gomberg and Schoepfle, *THIS JOURNAL*, 39, 1661 (1917).

oxygen absorption, so that the qualitative test of decolorization with oxygen is misleading unless accompanied by the quantitative measure of absorption.

Using ether as solvent, chloride and silver were shaken one hour. On working up in the usual manner, a dark oil was obtained which changed to light red crystals in the course of a day. These crystals could not be redissolved in a large quantity of ether, showing that the original soluble product was no longer present. Redissolved in benzene and treated with petroleum ether, they formed a light pink precipitate without crystalline structure. This material did not absorb oxygen, did not contain chlorine, and did not melt under 240°.

Since bromobenzene solutions appeared to be relatively stable, these were used with a 30-minute shaking period. To avoid the high temperature otherwise necessary to distil the solvent, distillation was dispensed with altogether. A large amount of petroleum ether was added to the solution precipitating a red-brown amorphous mass, which when washed with ether, became light pink. The test for oxygen absorption was made on the final dry product within 5 hours from the beginning of the experiment, but no oxygen was absorbed.

The procedure of Schlenk and Renning<sup>1</sup> was next duplicated. Copper bronze ("Naturkupfer C," which they also had used) was washed with alcohol and with ether, and dried in a stream of hydrogen at 250° for 3 hours. Its efficiency was demonstrated by preparing triphenylmethyl in boiling benzene solution under exactly the same conditions used later for phenyl-thio-xanthyl. 4.4 g. of pure phenyl-thio-xanthienol chloride and 20 g. of copper bronze were placed in a flask and protected by an atmosphere of carbon dioxide. Sixty cc. of dry thiophene-free benzene was admitted and heated to the boiling temperature in a glycerine bath. A stream of dry carbon dioxide was passed through the apparatus during the whole time of heating. Ten minutes was required to bring the benzene to boiling, heating was continued for 45 minutes and the red-brown solution was filtered into the free radical apparatus, together with 15 cc. of warm benzene. The solvent was evaporated under reduced pressure to  $\frac{1}{3}$  its volume and cooled. Since no precipitate appeared, petroleum ether was added and cooling continued overnight. Only a slight deposit of dark red-brown crystals had formed by the next morning, so a large quantity of petroleum ether was used, which threw down a pink amorphous solid. The mother liquor was removed and the product dried at room temperature in a stream of carbon dioxide. Yield, 3.0 g.

Oxygen absorption: 0.5763 g. of substance in xylene solution absorbed 1.3 cc. (N. T. P.) of oxygen, which is 5.5% of the calculated absorption for pure free radical.

The experiment was repeated with the precipitation of the product with petroleum ether immediately after partial evaporation of the solvent, so

that the oxygen absorption was measured 4 hours from the beginning of the operation. The product did not absorb oxygen.

The material obtained in this manner is soluble in benzene, xylene, chloroform and carbon disulfide, giving rich wine-red solutions; it is slightly soluble in warm acetone and is insoluble in ether, petroleum ether and gasoline. Several reprecipitations from benzene solution by petroleum ether gave a colorless amorphous solid, which decomposed at  $300^{\circ}$  to  $302^{\circ}$ . It is apparently identical with the products obtained under the other procedures. In no case could any peroxide be isolated.

As a final check upon the possibility of making the free radical by this last method, oxygen absorptions were taken on benzene solutions of chloride which had been boiled with copper bronze. At the end of the heating period the tubes containing the solutions were filled with benzene, cooled to room temperature and sealed. During the entire operation the solutions were under an atmosphere of dry hydrogen. The following measurements were made.

1.0169 g. of chloride, boiled for one hour, absorbed 25.2 cc. (N. T. P.) of oxygen, or 68.3% of the calculated quantity.

0.6516 g. of chloride, boiled for one hour, then allowed to stand for two hours at room temperature, absorbed 15.7 cc. (N. T. P.) of oxygen, or 66.5%.

0.7475 g. of chloride, boiled for three hours, absorbed 12.8 cc. (N. T. P.) oxygen, or 47.2%.

From these experiments we are inclined to conclude that the material obtained by Schlenk and Renning was not the free radical, phenyl-thio-xanthyl; and we believe that their values for the molecular weight and degree of dissociation of this radical should be rejected.

This investigation was made with the assistance of The National Aniline and Chemical Company Fellowship. We wish to express our obligations for the aid we have thus received.

### Summary.

The preparation of pure phenyl-thio-xanthenol chloride has been described. The free radical, phenyl-thio-xanthyl, has been prepared in solution and found to be very unstable, the rate of decomposition varying with the nature of the solvent. The radical could not be isolated in the solid state. It has been shown that the values obtained by Schlenk and Renning for the molecular weight of this substance were made on material which was in all probability not the free radical.



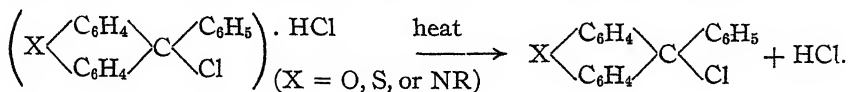
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.]

## 2,2'-SULFONIDO-TRIPHENYLMETHYL.

BY M. GOMBERG AND E. C. BRITTON.

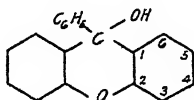
Received June 8, 1921.

The chlorides of aryl xanthenols, aryl thio-xanthenols and aryl acridols are prepared from their corresponding hydrogen chloride additive compounds,<sup>1</sup> in which however the acid is held with considerable tenacity.

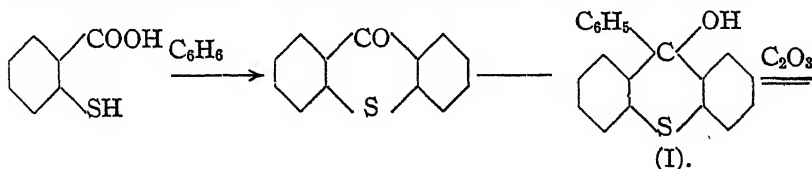


These normal chlorides are difficult to prepare in the pure state; the merest trace of moisture hydrolyzes them into carbinol and hydrochloric acid, the latter not escaping but being retained as the hydrochloride additive compound with the unhydrolyzed portion. In the process of the conversion of the carbinol chloride, contaminated in this manner, into the corresponding free radical the hydrogen chloride becomes liberated and tends to cause catalytic polymerization of the free radical. Herein may lie the reason why with this class of chlorides it has proved so difficult, and often wholly impossible, to isolate the free radical, notwithstanding the fact that the actual formation of the radical at the initial stage of the reaction could be demonstrated.

It seemed desirable to prepare a carbinol of bridged-ring type that would readily yield a stable chloride, one that would be devoid of the tendency to take on hydrogen chloride. Such a carbinol was found in 2,2'-sulfonido-triphenyl carbinol.<sup>2</sup>

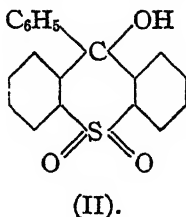


**2,2'-Sulfonido-triphenyl Carbinol, (Formula II).**—This was synthesized by the following set of reactions: thio-xanthone, prepared by the condensation of thiosalicic acid and benzene in presence of sulfuric acid, was allowed to react with phenyl magnesium bromide, and the thio-xanthenol thus formed was oxidized to the sulfone.



<sup>1</sup> Gomberg and Cone, *Ann.*, 370, 142 (1909); 376, 183 (1910).

<sup>2</sup> The nomenclature here adopted is analogous to that suggested for phenyl-xanthenol, namely, 2,2'-oxido-triphenyl carbinol. Meyer and Jacobson's "Lehrbuch d. org. Chemie" Veit and Company, [II] 1914, Part 3, p. 765.



The thio-salicylic acid was prepared from anthranilic acid<sup>3</sup> with a yield of 80% to 90%. Thio-xanthone was prepared according to Smiles.<sup>4</sup> Fifty g. of thio-salicylic acid, 500 cc. of conc. sulfuric acid and 150 cc. of benzene were stirred for 10 hours; the reaction mixture was allowed to stand for 10 hours and finally heated for 1 hour on the water-bath. Water was then carefully poured over the surface of the acid and allowed to diffuse slowly, a procedure, we believe, first used by Graiebe. This gave a crystalline product which was easily filtered. The xanthone was purified by recrystallization from chloroform and then from acetic acid. Yield, 85%.

Phenyl thio-xanthenol (Formula I) was prepared from phenyl magnesium bromide and thio-xanthone,<sup>5</sup> and purified by recrystallization from petroleum ether, b. p. 100° to 110°. The yield of the pure product never fell below 90%.

For oxidation to the sulfone the following procedure was adopted. Twenty g. of phenyl-thio-xanthenol was dissolved in 140 cc. of hot glacial acetic acid, and 25.5 g. of chromic acid dissolved in 40 cc. of water was added at such a rate as to maintain the temperature above 100°. The reaction mixture was then heated for one hour on the water-bath; 50 cc. of hot water was added, and the solution was cooled. The precipitate was removed by filtration and was washed repeatedly with hot water to remove chromic acetate and chromic acid. For purification, the sulfonido compound was recrystallized from glacial acetic acid. Yield, 85%.

Hydrogen peroxide was tried as the oxidizing agent, but only a small quantity of the sulfone was produced, the chief product being a compound lower melting, presumably the sulfoxide, along with some benzophenone sulfone.

Another method for the preparation of the sulfone carbinol was devised, namely, the action of phenyl magnesium bromide on benzophenone sulfone. The benzophenone sulfone was prepared by the oxidation of thio-xanthone in acetic acid solution with 30% hydrogen peroxide according to the method of Ullmann.<sup>6</sup> 0.1 mol of powdered benzophenone sulfone was slowly added to an ether-benzene solution of 0.1 mol of phenyl magnesium bromide, and the solution was heated under a reflux condenser for one hour. The magnesium-bromide addition compound was decomposed by ice in the usual manner, and since the sulfone carbinol is insoluble in both ether and water, it was removed by filtration after neutralization of the magnesium hydroxide with hydrochloric acid. This method gives a 90% yield of fairly pure product, but the benzophenone sulfone which does not enter into reaction is not easily separated from the carbinol. For this reason, the first method of preparation is preferable.

*Analysis.* Calc. for  $C_{19}H_{14}O_3S$ : C, 70.77; H, 4.09; S, 9.95. Found: C, 70.67; H, 4.50; S, 9.93.

The sulfonido-triphenyl carbinol crystallizes in the form of needles and melts without decomposition at 224° to 5°. The compound is only slightly soluble in the

<sup>3</sup> Friedlander, 9, 542, Ger. pat. 205,450.

<sup>4</sup> Davis and Smiles, *J. Chem. Soc.*, 97, 1296 (1910).

<sup>5</sup> Gomberg and Cone, *Ann.*, 376, 203 (1910).

<sup>6</sup> Ullmann and Glenck, *Ber.*, 49, 2487 (1916).

usual organic solvents at ordinary temperature, although it can be recrystallized from a mixture of equal parts of chloroform and absolute alcohol. The sulfonido-carbinol dissolves in conc. sulfuric acid producing a red-brown solution, and may be recovered unchanged upon addition of water.

**2,2'-Sulfonido-triphenyl Methane,  $\text{SO}_2:(\text{C}_6\text{H}_5)_2:\text{CH}(\text{C}_6\text{H}_5)$ .**—Reduction with stannous chloride and hydrochloric acid converts the chloride into the methane compound, the sulfone group remaining unaltered. Two g. of the sulfonido carbinol was dissolved in 25 cc. of glacial acetic acid and reduced with 3 g. of stannous chloride dissolved in 25 cc. of acetic and 3 cc. of hydrochloric acid. The mixture was heated for 1 hour on the water-bath, diluted with 10 cc. of hot water, and then allowed to crystallize. The sulfonido methane was recrystallized from glacial acetic acid and was obtained in the form of colorless needles, m. p.  $193^\circ$  to  $194^\circ$ . The yield of pure product was 1.7 g. No color is developed by treating the methane with conc. sulfuric acid; it is not acted upon by phosphorus pentachloride nor is it oxidized back to the carbinol by chromic acid in acetic acid solution.

*Analysis.* Calc. for  $\text{C}_{19}\text{H}_{14}\text{O}_2\text{S}$ : S, 10.47. Found: 10.49.

**2,2'-Sulfonido-triphenyl Carbinol Chloride,  $\text{SO}_2:(\text{C}_6\text{H}_5)_2:\text{C}(\text{C}_6\text{H}_5)\text{Cl}$ .**—The carbinol chloride cannot be obtained by treating the carbinol with hydrogen chloride in ether or benzene solution, nor by boiling with acetyl chloride, thionyl chloride, or phosphorus trichloride, whereas practically nearly all the triaryl carbinols are converted to the corresponding chlorides by such treatment. Twenty g. of the carbinol was intimately mixed with slightly more than the theoretical quantity of phosphorus pentachloride (1 g. in excess) and the mixture was heated in an oil-bath at  $110^\circ$  to  $120^\circ$ . When the evolution of hydrogen chloride had commenced, the flask was removed from the oil-bath until the evolution of the gas had practically ceased, and the mixture was further heated for  $\frac{1}{2}$  hour. The phosphorus oxychloride was then distilled and the excess of phosphorus pentachloride was volatilized under reduced pressure by means of a current of dry air. The residue was dissolved in 75 cc. of hot benzene, filtered from some red precipitate, and the carbinol chloride was precipitated by the addition of 80 cc. of dry ligroin. For purification, the chloride was recrystallized from high-boiling ligroin ( $100^\circ$  to  $10^\circ$ ), the accompanying red impurity being entirely insoluble in this solvent, while the chloride is soluble to the extent of about 2 g. in 100 cc. Yield of pure product, 80%.

*Analysis.* Calc. for  $\text{C}_{19}\text{H}_{13}\text{O}_2\text{SCl}$ : C, 66.94; H, 3.84; S, 9.41; Cl, 10.41. Found: C, 66.65; H, 3.88; S, 9.42; Cl, 10.41.

The sulfonido-chloride melts without decomposition at  $160^\circ$  to  $1^\circ$ . It is readily soluble in benzene, chloroform, acetone, carbon tetrachloride, ethyl acetate, slightly soluble in ether, carbon disulfide, and practically insoluble in cold ligroin. It can be converted quantitatively into the carbinol by boiling with 80% acetic acid or diluted alcohol.

**The Free Radical, 2,2'-Sulfonido-triphenylmethyl  $\text{SO}_2:(\text{C}_6\text{H}_5)_2:\text{C}(\text{C}_6\text{H}_5)$ .**—The carbinol chloride employed for the preparation of the free radical was the purest possible, checked by its melting point and analysis. After many trials the following procedure was adopted. Two g. of the sulfonido-chloromethane and 12 g. of molecular silver (100 mesh) were placed in a 75cc. bottle, and enough benzene was added almost to fill the bottle, which was then tightly stoppered. After 35 minutes of vigorous shaking, the benzene solution was filtered into the standard apparatus,<sup>7</sup>

<sup>7</sup> Gomberg and Schoëpfle, *THIS JOURNAL*, 39, 1659 (1917)

and concentrated under reduced pressure at a temperature of 40°. Fifteen cc. of ether was then added to the sirupy residue in small portions, with shaking after each addition, and the free radical allowed to crystallize. After standing for 1 hour at 0°, the solvent was drawn off, the crystals were washed with ether and dried at a temperature of 40° for 1 hour. The yield of pure product was 1 to 1.3 g.

The free radical appears as a slightly yellow crystalline powder, which melts with decomposition at about 180°. It is soluble in all the usual organic solvents with the exception of ether, carbon disulfide, and ligroin, giving orange colored solutions, lighter in color than those of the radical phenyl-thio-xanthyl. When the free radical was recrystallized from carbon disulfide, the crystals formed did not lose all the carbon disulfide at any temperature below 80°, even under reduced pressure. Presumably a combination of free radical and solvent had occurred.

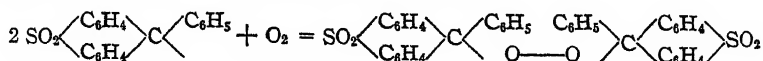
Calc. for  $C_{18}H_{18}O_2S$ : S, 10.50. Found: 10.57.

The procedure outlined above must be followed exactly in order to obtain a fair yield. If the weight of the silver is decreased, all of the carbinol chlorine will not be removed in a sufficiently short time, the same difficulty occurring if the silver is coarser than 100 mesh. If the time of shaking is prolonged, the product will absorb less than the theoretical quantity of oxygen, indicating decomposition of free radical. Indeed, shaking for one day with the quantities indicated will give a product entirely incapable of absorbing oxygen. Further than this, the free radical even in the solid state cannot be heated above 40° for any length of time without suffering some change.

**Oxygen Absorption and the Peroxide.**—When a solution of the free radical is exposed to oxygen or air a crystalline peroxide is formed and the solution becomes decolorized. The yield of the peroxide is usually 80 to 85%, just as has been found to be the case with triphenylmethyl and a number of other free radicals. The peroxide is insoluble in nearly all the organic solvents except chloroform, in which it is readily soluble, and benzene, in which it is slightly soluble. It crystallizes in the form of colorless needles, which melt with decomposition at 238° to 9°. It may be converted into the carbinol by heating at 100° with conc. sulfuric acid, the yield of carbinol amounting to about 40%.

Calc. for  $C_{38}H_{26}O_6S_2$ : C, 70.97; H, 4.08; S, 9.99. Found: C, 70.22; H, 4.26; S, 9.99.

In the formation of the sulfonido-triphenylmethyl peroxide from a solution of free radical the theoretical amount of oxygen is absorbed, two mols of the radical uniting with one mol of oxygen.



Oxygen absorptions were taken on the free radical produced in solution directly from the chloride as well as upon the previously isolated crystalline compound. In the former instance, the chloride was dissolved in bromobenzene, shaken with silver for 35 minutes in a sealed tube, and the absorption then taken after breaking the tube in the absorption apparatus connected with the gas buret. In addition, the yield of the peroxide formed was determined in each experiment.

Wt. of sample.		Cc	Oxygen. % of calc.	G.	Peroxide. % of calc.
Chloride.	Free Rad.				
0.5000	....	16.2	99.0	0.3700	79.0
0.5000	....	16.0	97.0	0.3500	74.5
0.5000	....	16.0	97.0	0.3645	77.5
....	0.4525 <sup>a</sup>	15.3	92.0	0.3522	74.0
....	0.7110	26.1	100.0	0.5920	79.0
....	0.8567	30.0	96.5	0.7390	80.7

<sup>a</sup> Absorption taken in benzene.

**Iodine Absorption.**—By adding a standard benzene solution of iodine to a benzene solution of the free radical, a titration may be accomplished, although the end point is rather indistinct, being observed in a brown solution. Two samples, 1.1000 and 0.7568 g. absorbed 0.412 and 0.298 g. of iodine, equivalent to 90.0 and 99.0%, respectively.

No attempts were made to isolate the unstable iodide. When the solution of the iodide is allowed to stand in air, iodine is liberated and large amounts of peroxide are formed.

**Molecular Weight Determination.**—Similar apparatus and manipulation were employed by us in the determination of the molecular weight of the free radical as previously described.<sup>8</sup> The samples used for the molecular weight determinations were all carefully dried under reduced pressure in an atmosphere of carbon dioxide at the temperature of boiling ether, and were in an inert atmosphere except during the short period of weighing. The determinations were carried out in an atmosphere of hydrogen to prevent oxidation of the free radical. Every sample to be used was analyzed as to its purity, and none was used which did not indicate an absorption of oxygen above 95% of that calculated. But two solvents were used, namely benzene and *p*-bromotoluene, giving temperatures of 5.4° and 27° respectively. The molecular depression constant for benzene was taken as 50 and for *p*-bromotoluene as 82.

At the completion of each molecular-weight determination the solution was exposed to air and the amount of peroxide formed showed that the radical had undergone practically no change in the process of the molecular-weight determination.

The results given in the following table indicate that there is little change in the molecular weight with increase in temperature from 6° to 27°, but there

<sup>8</sup> Gomberg and Schoepfle, *THIS JOURNAL*, 39, 1662 (1917).

Solvent.	Wt. of solvent. G.	Wt. of free radical. G.	Concentration. %.	Depression of f. p.	Mol. wt.
Benzene	17.42	0.1733	0.98	0.106	469.3
	...	0.3335	1.88	0.194	493.4
	...	0.5120	2.85	0.279	526.7
	17.14	0.1900	1.10	0.126	450.1
	...	0.3446	1.97	0.212	474.2
	...	0.5231	2.96	0.305	500.3
	17.20	0.2140	1.23	0.130	478.5
	...	0.3210	1.83	0.188	496.3
	...	0.4242	2.41	0.247	520.3
	...	0.2612	1.31	0.257	424.9
<i>p</i> -Bromotoluene	19.61	0.2612	1.31	0.257	424.9
	...	0.4563	2.27	0.388	491.8
	...	0.6309	3.12	0.528	499.6
	19.82	0.1800	0.90	0.167	446.0
	...	0.3427	1.70	0.292	485.6
	...	0.4453	2.20	0.366	503.3

is a remarkable change with increasing concentrations, the latter change however being somewhat irregular, and the results are possibly not so accurate as might be wished. The free radical, in solution, is evidently monomolecular to the extent of 30 to 38%, and dimolecular to 62 to 70%.

### Summary.

1. 2,2'-Sulfonido-triphenyl carbinol and the corresponding chloride were prepared. It was found that this chloride, unlike the chlorides of aryl thio-xanthenols, does not make additive colored compounds with hydrogen chloride.

2. The free radical, 2,2'-sulfonido-triphenylmethyl, was prepared. Its oxygen absorption, the degree of combination with iodine, and extent to which it exists as monomolecular have been determined.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO.]

## THE FRIEDEL AND CRAFTS' REACTION. BROMOPHTHALIC ANHYDRIDES, BENZENE AND ALUMINUM CHLORIDE.

BY H. N. STEPHENS.

Received June 8, 1921.

Rubidge and Qua<sup>1</sup> have studied the reaction between phthalic anhydride, benzene and aluminum chloride and have shown the conditions which will give a good yield of *o*-benzoyl-benzoic acid, and also the conditions which will give no acid and a 35% yield of diphenylphthalide. Lawrance,<sup>2</sup> who used the nitrophthalic anhydrides and the acetyl-amino-phthalic anhydrides in this reaction, points out that from each substituted phthalic anhydride there are possible two acid products and two derivatives of diphenyl-phthalide.

<sup>1</sup> Rubidge and Qua, THIS JOURNAL, 36, 732 (1914).

<sup>2</sup> Lawrance, *ibid.*, 42, 1871 (1920).

Two investigators have previously prepared *o*-benzoyl-bromobenzoic acid by this method. In 1879, nine years before Friedel and Crafts published their paper on the preparation of *o*-benzoyl-benzoic acid, Pechman<sup>3</sup> heated a mixture of bromophthalic anhydrides with benzene and aluminum chloride and obtained a product which he called *o*-bromobenzoyl-benzoic acid, m. p. 219° to 221°. This product was probably an impure specimen of 6-benzoyl-2-bromobenzoic acid, m. p. 231.5°. It will be noticed that, as Pechman used a mixture of the two bromophthalic anhydrides, there would be four possible products while he only described one. The results of the other investigator are given in a German patent.<sup>4</sup> He obtained two *o*-benzoyl-bromobenzoic acids, one from bromophthalic acid, an excess of aluminum chloride being used to dehydrate the acid, and the other from bromophthalic anhydride. The product from the latter melted at 174° and corresponds to that obtained by Kohler, Heritage and Burnley<sup>5</sup> by the oxidation of 2,6-dibromo-3-keto-1-phenyl-2,3-dihydrindene. As this product has been obtained in the present investigation from 4-bromophthalic anhydride and as the other product (m. p. 216° to 219°) more closely resembles the product from the 3-bromophthalic anhydride it might be inferred that a mixture of the bromophthalic acids was used in this case also. The present investigation was for the purpose of preparing and identifying the various *o*-benzoyl-bromobenzoic acids and the diphenyl-bromophthalides.

**3-Bromophthalic Acid.**—This acid has been prepared by Faust,<sup>6</sup> Pechman,<sup>3</sup> and Smith<sup>7</sup> but in each case the melting point is much too low and the product is evidently a mixture. Guareschi<sup>8</sup> oxidized 5-bromo-1-nitronaphthalene with potassium permanganate and obtained an acid melting at 174° to 176° but this method gave the writer only a 4% yield and the reduction of the 5-bromo-1-nitronaphthalene to 5-bromo-1-aminonaphthalene before oxidation did not improve the yield. The method finally adopted was the conversion of 3-aminophthalic acid into 3-bromophthalic acid by the Sandmeyer method. The aminophthalic acid was prepared as described by Lawrence.

Twenty-five g. of 3-nitrophthalic acid was reduced and the hydrochloride of the amino acid mixed with 200 cc. of 18% hydrochloric acid, diazotized, and poured into 150 cc. of a warm 10% solution of cuprous bromide. After warming gently on the water-bath to drive off oxides of nitrogen the solution was allowed to stand for several hours and a precipitate of *o*- and *m*-bromobenzoic acids was then filtered off and the filtrate extracted with ether, affording a yield of 28%. In this reaction a reddish oil is fre-

<sup>3</sup> Pechman, *Ber.*, 12, 2126 (1879).

<sup>4</sup> Gesellschaft für Anilin Fabrikation.

<sup>5</sup> Kohler, Heritage and Burnley, *Am. Chem. J.*, 44, 60 (1910).

<sup>6</sup> Faust, *Ann.*, 160, 62 (1871).

<sup>7</sup> Smith, *J. Chem. Soc.*, 35, 792 (1879).

<sup>8</sup> Guareschi, *Ann.*, 222, 292 (1884).

quently obtained which may be removed by dissolving the acid in potassium hydroxide and oxidizing with potassium permanganate. The acid, recrystallized from water, melts at 177° to 8°.

*Analysis.* Calc. for  $C_8H_4O_4Br$ : Br. 32.6. Found: 32.4.

The anhydride was prepared from the acid by distillation and recrystallization from glacial acetic acid, m. p. 130–1°.

**4-Bromophthalic Acid.**—Nourrisson<sup>9</sup> prepared this acid from bromo-*o*-toluidine by converting it into the nitrile, hydrolyzing the nitrile and oxidizing the resulting bromo-*o*-toluic acid. Miersch<sup>10</sup> obtained the acid by oxidizing *p*-bromohydrindene with 25% nitric acid, and Perkin and Revay<sup>11</sup> oxidized bromo-indene with dil. nitric acid. The method finally adopted was that described by Armstrong and Rossiter<sup>12</sup> who oxidized 1,6-dibromo-2-naphthol and obtained a small quantity of 4-bromophthalic acid but give no quantitative details.

One hundred g. of  $\beta$ -naphthol was dissolved in 500 cc. of glacial acetic acid and a mixture of 223 g. of bromine and 100 cc. of acetic acid added. After standing overnight the crystals were filtered off, washed with water and dried in a vacuum oven at 70° for one hour. Evaporation of the mother liquor yielded more of the product. Recrystallized from 80% acetic acid the dibromo-naphthol melts at 106°; yield 90%.

Sixty g. of dibromonaphthol was dissolved in 1200 cc. of water containing 20 g. of potassium hydroxide, and 160 g. of potassium permanganate was added gradually with constant stirring, the temperature being kept low. After standing for 3 or 4 hours the solution was heated on the water-bath and potassium permanganate added gradually until a permanent pink color was obtained. The solution was then decolorized with ferrous sulfate, filtered, evaporated to 400 cc., acidified and extracted with ether. The product when recrystallized from water containing a few drops of sulfuric acid, melted at 170.5° and the yield of crude acid was 47% calculated on the dibromo-naphthol. The anhydride was prepared by distilling the acid; yield, 80%. The distillate was a white, crystalline mass, m. p. 104° to 106°. No solvent was found from which it could be recrystallized. On standing it changed slowly back to the acid.

### Reaction of 3-Bromophthalic Anhydride with Benzene and Aluminum Chloride.

Four and three-tenths g. of powdered 3-bromophthalic anhydride, 12 cc. of benzene and 5 g. of aluminum chloride were boiled for 4 hours on the water-bath under a return condenser. After the addition of 100 cc. of 10% hydrochloric acid the benzene was distilled with steam and the precipitate digested with a hot solution of sodium carbonate which left a slight residue of phthalide. The solution was diluted to about 250 cc. and very slowly acidified with 5% hydrochloric acid. If the acid is precipitated rapidly it separates as a gum which becomes crystalline only on long standing. The dry product was dissolved in 75 cc. acetone, 60 cc.

<sup>9</sup> Nourrisson, *Ber.*, 20, 1016 (1887).

<sup>10</sup> Miersch, *ibid.*, 25, 2115 (1892).

<sup>11</sup> Perkin and Revay, *J. Chem. Soc.*, 65, 253 (1894).

<sup>12</sup> Armstrong and Rossiter, *Ber.*, 24, ref. 705 (1891).



water added and the solution left overnight to crystallize. After several recrystallizations a constant melting point,  $231.5^{\circ}$ , was obtained. This substance is the only acid product of the reaction and is probably identical with the substance described by Pechman, m. p.  $219-21^{\circ}$ ; yield, 89%, calculated on the bromophthalic anhydride.

**Identification of the Substance Melting at  $231.5^{\circ}$ .**—Eight g. of potassium hydroxide was dissolved in a little water in a nickel crucible and 1 g. of the substance added. The mixture was slowly heated on a sand-bath, with constant stirring, and held at  $220-5^{\circ}$  for 25 minutes. After dissolving in water and acidifying, the precipitate contained benzoic acid and *o*-bromobenzoic acid. The substance is therefore, 6-benzoyl-2-bromobenzoic acid.

Calc. for  $C_{14}H_9O_3Br$ : Br, 26.2. Found: 26.1.

### Reaction of 4-Bromophthalic Anhydride with Benzene and Aluminum Chloride.

Four and three tenths g. of 4-bromophthalic anhydride, 12 cc. of benzene and 5 g. of aluminum chloride were boiled for 6 hours. The product of the reaction was obtained as in the previous experiment. The greenish gum given by the slow acidification of the sodium carbonate solution became crystalline on standing for a few hours; yield, 97%. The precipitate was washed, dried, dissolved in 40 cc. of alcohol, and water added just to turbidity. After standing for 12 hours in a covered dish the precipitate was filtered off and a second precipitate obtained by allowing the filtrate to stand for a day in an open dish.

After several recrystallizations the first fraction gave flat needles, soluble in ether and acetone, moderately soluble in alcohol, slightly soluble in hot benzene and insoluble in ligroin; m. p.  $193^{\circ}$ . This fraction was about 55% of the total yield of acids. The second fraction, after several recrystallizations, gave small rhombohedrons, m. p.  $172.5^{\circ}$ , very soluble in alcohol, ether and acetone, slightly soluble in hot benzene and insoluble in ligroin. This substance is, no doubt, identical with that described by Kohler, Heritage and Burnley<sup>5</sup> (m. p.  $174^{\circ}$ ) and with that described in the German patent.<sup>4</sup> This fraction represents about 45% of the total yield of acids.

**Identification of the Substance Melting at  $193^{\circ}$ .**—The substance was hydrolyzed by fusing with potassium hydroxide for 10 minutes at  $185-90^{\circ}$ . The fusion products were benzoic acid and *p*-bromobenzoic acid, and the substance is therefore 2-benzoyl-4-bromobenzoic acid.

Calc. for  $C_{14}H_9O_3Br$ : Br, 26.2. Found: 26.3.

**Identification of the Substance Melting at  $172.5^{\circ}$ .**—In the fusion of this substance the temperature was kept at  $170-5^{\circ}$  for 20 minutes. The fusion products were benzoic acid and *m*-hydroxybenzoic acid. As

*m*-bromobenzoic acid is changed to *m*-hydroxybenzoic acid by fusion with potassium hydroxide this identifies the substance as 6-benzoyl-3-bromobenzoic acid although Kohler, Heritage and Burnley described it as *p*-bromo-*o*-benzoylbenzoic acid.

### Reaction of 3-Bromophthalic Anhydride with Benzene, Aluminum Chloride and Acetic Anhydride.

Four and three tenths g. of 3-bromophthalic anhydride, 12 cc. of benzene and 5 g. of aluminum chloride were boiled for 4 hours and then 3 cc. of acetic anhydride and an additional 12 cc. of benzene were added, and boiling was continued for 3 hours. After treatment with sodium carbonate only a small quantity of insoluble material remained which on recrystallization from benzene melted at 148–50°.

As 3-bromophthalic anhydride gave only 6-benzoyl-2-bromobenzoic acid, only the diphenyl-bromophthalide corresponding to this acid is to be expected in the above reaction.

### Diphenyl-3-Bromophthalide.

Pechman<sup>13</sup> prepared diphenyl-phthalide from the mixed anhydride of *o*-benzoyl-benzoic acid and acetic anhydride with benzene and aluminum chloride. Following Pechman's method the anhydride of 6-benzoyl-2-bromobenzoic acid and acetic acid was prepared and then from it the corresponding diphenyl-bromophthalide.

Two g. of 6-benzoyl-2-bromobenzoic acid was heated on a water-bath with 4 cc. of acetic anhydride for 12 hours, and the liquid then poured into an equal volume of 95% alcohol. On standing for several hours a white crystalline substance separated which on recrystallization from alcohol gave fine colorless needles; m. p. 168.5°.

*Analysis.* Calc. for  $C_{16}H_{11}O_4Br$ : Br, 23.05. Found: 22.9.

One g. of this anhydride was heated with 5 cc. of benzene and 0.8 g. of aluminum chloride for 6 hours. After acidification the benzene was distilled with steam and the solid heated with sodium carbonate solution to remove acids. The insoluble residue was recrystallized from benzene and then from alcohol; m. p. 131°; yield, 71%.

*Analysis.* Calc. for  $C_{20}H_{13}O_2Br$ : Br, 21.9. Found: 20.4.

The very small quantity of the product, m. p. 148–50°, obtained from the 3-bromophthalic anhydride with benzene, aluminum chloride and acetic anhydride is not, therefore, diphenyl-3-bromophthalide.

### Reaction of 4-Bromophthalic Anhydride with Benzene, Aluminum Chloride and Acetic Anhydride.

Four and three tenths g. of 4-bromophthalic anhydride, 12 cc. of benzene and 5 g. of aluminum chloride were boiled for 6 hours, and then 3 cc. of

<sup>13</sup> Pechman, *Ber.*, 14, 1865 (1881).

acetic anhydride and 12 cc. of benzene were added and the boiling continued for 3.5 hours. After treatment with sodium carbonate the insoluble residues (diphenyl-bromophthalides) represented a total yield of 60%. This product was dissolved in a small amount of benzene and after standing for 24 hours gave a thick reddish liquid and a crystalline mass. The crystals after several recrystallizations from benzene melted at 186°. The reddish liquid was heated in a vacuum oven to remove benzene and the hard gummy residue was dissolved in a small quantity of hot alcohol, which on cooling deposited a reddish gum, but the remaining liquid after several hours gave a white crystalline substance which after several recrystallizations from methyl alcohol melted at 115–6°.

**Identification of the Diphenyl-bromophthalide, m. p. 186°.**—Two g. of 2-benzoyl-4-bromobenzoic acid was heated with 4 cc. of acetic anhydride for 4 hours on the water-bath. The solution was then poured into an equal volume of 80% alcohol and allowed to stand for several hours, when a gummy substance separated which on solution in hot alcohol, and cooling, gave a white amorphous powder; m. p. 83–7°. This powder with benzene and aluminum chloride gave a product, m. p. 186°, identical with one of those obtained from the 4-bromophthalic anhydride. It is, therefore, diphenyl-5-bromophthalide. Yield, 56%.

Calc. for  $C_{20}H_{13}O_2Br$ : Br, 21.9. Found: 21.8.

**Identification of the Diphenyl-bromophthalide, m. p. 115.6°.**—Two g. of 6-benzoyl-3-bromobenzoic acid was heated on the water-bath for 6 hours with 4 cc. of acetic anhydride. The product was then poured into double its volume of hot 50% alcohol and an oil separated on cooling. This oil did not crystallize after several precipitations from hot methyl alcohol but hardened to a gum with no definite melting point when dried *in vacuo*. This gum with benzene and aluminum chloride gave a product, m. p. 115–6°, identical with the product from 4-bromophthalic anhydride, benzene and aluminum chloride. It is, therefore, diphenyl-4-bromophthalide. Yield of crude material, 69%.

Calc. for  $C_{20}H_{13}O_2Br$ : Br, 21.9. Found: 22.1.

When 3-bromophthalic anhydride reacts with benzene and aluminum chloride only 6-benzoyl-2-bromobenzoic acid is obtained but when 4-bromophthalic anhydride is used approximately equal quantities of 2-benzoyl-4-bromobenzoic acid and 6-benzoyl-3-bromobenzoic acid are formed. The total yield in each case is good. The fact that only one product is obtained from 3-bromophthalic anhydride might be due to steric hindrance but Mr. Lawrance, in this laboratory, has found that the tetrahalogen-phthalic anhydrides with benzene and aluminum chloride give good yields of the benzoyl-tetrahalogen-benzoic acids.

Using benzene, aluminum chloride and acetic anhydride, 3-bromophthalic anhydride gave no diphenyl-bromophthalide, while a good yield

of both the possible diphenyl-bromophthalides was obtained from 4-bromophthalic anhydride. Oddy, working at McMaster University, has obtained good yields of the diphenyl-tetrahalogen-phthalides from the tetrahalogen-phthalic anhydrides.

### Summary.

1. Each of the two bromophthalic anhydrides has been found to react with benzene and aluminum chloride forming benzoyl-bromobenzoic acids. The 3-anhydride yielded only one acid while the 4-anhydride gave two in approximately equal quantities.

2. Under the conditions favorable to the production of diphenyl-bromophthalides, the 3-anhydride gave no diphenyl-bromophthalide while the 4-anhydride gave two.

3. A new method is described for the preparation of 3-bromophthalic acid and detailed directions given for the preparation of 1,6-dibromo-2-naphthol and 4-bromophthalic acid.

4. Seven new compounds have been prepared: 2-benzoyl-4-bromobenzoic acid, m. p. 193°; diphenyl-3-bromophthalide, m. p. 131°; diphenyl-4-bromophthalide, m. p. 115-6°; diphenyl-5-bromophthalide, m. p. 186°; mixed anhydride of 6-benzoyl-2-bromobenzoic acid and acetic acid, m. p. 168.5°; mixed anhydride of 2-benzoyl-4-bromobenzoic acid and acetic acid, m. p. 83-7°; and mixed anhydride of 6-benzoyl-3-bromobenzoic acid and acetic acid.

This research was carried out under the direction of Professor F. B. Allan. The writer held a bursary from the Honorary Advisory Council for Scientific and Industrial Research.

TORONTO, CANADA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY,  
No. 372.]

## THE ACTIVITY OF ADSORBED INVERTASE.

BY J. M. NELSON AND DAVID I. HITCHCOCK.

Received June 8, 1921.

The action on sucrose solutions of invertase adsorbed on charcoal and on gelatinous aluminum hydroxide was studied by Nelson and Griffin<sup>1</sup>. They reported that in their experiments a given quantity of enzyme exhibited the same activity when adsorbed on a solid in the bottom of the reaction vessel as when uniformly distributed throughout the solution. The importance of this observation and its bearing on the true nature of  
<sup>1</sup>Nelson and Griffin, *THIS JOURNAL*, 38, 722, 1109(1916).

enzyme action have been pointed out by Bayliss<sup>2</sup>, Lewis<sup>3</sup>, Falk<sup>4</sup> and others, and have led to the present further study of this phenomenon.

In some preliminary experiments with different charcoals it was found that in all cases where the invertase was completely adsorbed (or nearly so) there was a marked retardation of the hydrolysis. One charcoal was tried which caused very little retardation, but it was found that in this case the invertase was adsorbed only to a small extent. In order to determine whether the invertase was largely adsorbed or not, a mixture of sugar solution, adsorbent and invertase was prepared, shaken, and filtered about 10 or 15 minutes after the addition of the invertase. The absence of further change in the optical rotation of the filtrate indicated that the invertase had been completely adsorbed; much change in the rotation of the filtrate indicated incomplete adsorption. The retardation observed in the presence of the adsorbent could not have been due to changes in the hydrogen-ion concentration, since this was kept constant in all the experiments, both with and without adsorbent, by means of buffers. The result of a typical experiment with a charcoal of good adsorbing power are given in Table I.

TABLE I.  
Change in rotation.

Time, hours.	Filtrate.	Control (no charcoal).	Solution with charcoal.
18	0.40°	7.14°	2.03°
25.3	0.64	8.21	2.59
42.3	0.91	8.94	3.68

On testing the activity of invertase adsorbed on aluminum hydroxide, it was found that here too there was considerable retardation. It was thought that this might be due to the mechanical removal of the enzyme from the solution by the settling of the adsorbent. To test this explanation a mechanical stirrer was employed, which prevented the aluminum hydroxide from settling. It was found that the stirring prevented the greater part of the retarding action, as is shown by the results in Table II.

TABLE II.

Expt.	Sucrose conc., g. per 100 cc.	Time. Hours.	Filtrate.	Change in rotation.		
				Control.	With Al(OH) <sub>3</sub> . Stirred.	Not stirred.
20	5	1	0.00°	4.23°	3.82°	2.25°
21	10	1	0.01	4.53	4.18	3.61

From these experiments it was concluded that when an adsorbent is used without stirring, the rate at which the sucrose reaches the invertase is governed by the rate of diffusion of the sucrose down to the bottom of the vessel. Accordingly it was thought that if the action of the invertase

<sup>2</sup> Bayliss, "The Nature of Enzyme Action," 4th Ed., 1919, p. 112.

<sup>3</sup> Lewis, "A System of Physical Chemistry," 2nd Ed., Vol. I, 1918, p. 460.

<sup>4</sup> Falk, "The Chemistry of Enzyme Action," 1921, p. 61.

could be made even slower than the diffusion of the sucrose to the bottom of the reaction bottle, then there should be no retardation by the aluminum hydroxide. This was tried with 3 different invertase preparations by diluting the invertase to different degrees, with the results shown in Table III.

TABLE III.

Effect of Invertase Concentration on Retardation by Aluminum Hydroxide.

Expt.	Invertase conc. cc. per 100 cc. Prep. No. 1a	Time. Hours.	Filtrate.	Change in rotation.		Retardation by Al(OH) <sub>3</sub> , % of change in control.
				Control.	With Al(OH) <sub>3</sub> .	
22	2.50	18	0.00°	3.10°	2.78°	10
25	1.25	18	0.07	1.51	1.52	00
26	0.50	18	0.00	0.59	0.60	
Prep. No. 8.						
27	1.00	1	0.05	6.79	4.68	31
28	0.10	12	0.05	6.97	5.58	20
31	0.05	12	0.00	3.66	3.20	13
32	0.025	24	0.01	3.65	3.47	5
30	0.01	24	0.01	1.43	1.45	0
Prep. No. 10.						
41	2.50	24	0.11	3.83	3.38	12
43	1.25	24	0.05	1.38	1.29	7
44	0.50	24	0.02	0.75	0.73	3
44	0.50	48	0.01	1.38	1.37	1
44	0.50	96	0.01	2.45	2.47	0

It seems from these figures that the absence of retardation observed by Nelson and Griffin is not general, but represents only a very special case. Probably in most of their work the action of the enzyme was slower than the rate of diffusion of the sucrose. The slow rate of reaction in their second series of experiments<sup>5</sup> indicates that this explanation may apply there.

In some of the experiments with charcoal reported by Griffin and Nelson in their first paper,<sup>6</sup> the rate of reaction seems not to have been very slow. Since they gave no measurements of the inverting power of the filtrates in these experiments, it is possible that the absence of retardation may have been due to incomplete adsorption of the invertase by the charcoal. The present authors are unable to explain the earlier experiment<sup>7</sup> with aluminum hydroxide at hydrogen ion concentration  $5.0 \times 10^{-7}$  in which it was shown that the invertase was completely adsorbed. Repetitions of this experiment at about the same rate of inversion have indicated a retardation by aluminum hydroxide.

<sup>5</sup> *Loc. cit.*, p. 1110.

<sup>6</sup> *Ibid.*, p. 727.

<sup>7</sup> *Ibid.*, p. 729.

### Experimental Details.

**Materials.**—The invertase was prepared from yeast by the method of Nelson and Born<sup>8</sup> omitting the second and final precipitations by alcohol. Preparation 10 was obtained by dissolving 0.570 g. of the solid Invertase A of Nelson and Vosburgh<sup>9</sup> in 500 cc. of distilled water.

Suspensions of aluminum hydroxide prepared from the chloride could not be used; the precipitate so made either clogged the filter or ran through in a turbid colloidal suspension and did not completely adsorb the invertase. The aluminum hydroxide finally used was prepared from alum as described by Welker and Marshall,<sup>10</sup> and was washed repeatedly by decantation and also by dialysis for 2 days against running water. The suspension contained 0.0205 g. of aluminum oxide in 5 cc. In each experiment 100 cc. of the reaction mixture contained 5 cc. of this suspension.

The charcoal used in the experiment of Table I was an imported decolorizing powder; 100 cc. of the reaction mixture contained 0.30 g. of charcoal. In other experiments samples of this charcoal which had been boiled with hydrochloric acid or ammonium hydroxide and then washed caused the same retardation as the untreated charcoal.

The cane sugar was used the best commercial grade, as was that used by Nelson and Griffin.

**Control of the Hydrogen-ion Concentration.**—The buffer used in the experiments with charcoal was a mixture of secondary sodium citrate and hydrochloric acid.<sup>11</sup> It was found that the aluminum hydroxide did not completely adsorb the invertase in the presence of a citrate buffer at  $P_H = 4.45$  (or a phosphate buffer at  $P_H = 6.3$ ); accordingly for the experiments with aluminum hydroxide a buffer mixture of acetic acid and sodium acetate was prepared.<sup>12</sup> In all experiments the reaction mixture was 0.01 *M* with respect to total electrolyte. In the experiments of Tables I, II, III the hydrogen-ion concentration was  $10^{-4.4}$  to  $10^{-4.5}$  moles per liter, which is the optimum for invertase action.<sup>13</sup> The hydrogen-ion concentration was measured by the colorimetric method using  $\alpha$ -naphthyl-amino-azo-*p*-benzene sulfonic acid as indicator with citrate standards, which were standardized electrometrically using the saturated potassium chloride calomel cell.<sup>14</sup> The hydrogen-ion concentrations were based on 0.1000 *M* hydrochloric acid as a standard, its ionization<sup>15</sup> being taken as 91.7% at 37°.

**Procedure.**—The method of experimentation was similar to that of Nelson and Vosburgh,<sup>9</sup> but in accordance with the recommendation of Vosburgh<sup>16</sup> the dilution of the invertase with anything except water was avoided until the time for starting the reaction. The invertase was diluted with distilled water to twice the strength required, and to start the reaction, it was mixed with an equal volume of a double strength

<sup>8</sup> Nelson and Born, *THIS JOURNAL*, **36**, 393 (1914).

<sup>9</sup> Nelson and Vosburgh *ibid.*, **39**, 790 (1917).

<sup>10</sup> Welker and Marshall, *ibid.*, **35**, 822 (1909).

<sup>11</sup> Sorensen, *Compt. rend. Lab. Carlsberg*, **8** (1909); *Biochem. Z.*, **21**, 131 (1909).

<sup>12</sup> Michaelis, "Die Wasserstoffionenkonzentration," Berlin, 1914, p. 180.

<sup>13</sup> Fales and Nelson, *THIS JOURNAL*, **37**, 2770 (1915), and others.

<sup>14</sup> Fales and Mudge, *ibid.*, **42**, 2434 (1920).

<sup>15</sup> A. A. Noyes, "The Electrical Conductivity of Aqueous Solutions," 1907, p. 339.

<sup>16</sup> Vosburgh, "Some Errors in the Study of Invertase Action," *THIS JOURNAL*, **43**, 1693 (1921).

sugar solution containing buffer, either with or without charcoal or aluminum hydroxide. The concentration of sucrose in the reaction mixture was 10 g. per 100 cc., except in Table I and Expt. 20, Table II, where it was 5 g. per 100 cc. The inversions were allowed to take place in Nonsol glass bottles in a thermostat at  $37^{\circ} \pm 0.02^{\circ}$ . Bacterial action was avoided by keeping the solutions saturated with toluene. The reaction was stopped and mutarotation hastened by the use of sodium carbonate,<sup>17</sup> a 25cc. sample being added to 5 cc. of 0.1 *M* sodium carbonate solution. For the measurements of rotation the solutions were put into 200mm. tubes in the thermostat described by Nelson and Beegle,<sup>18</sup> which remained at  $25^{\circ} \pm 0.05^{\circ}$ . Readings were taken with a Schmidt and Haensch polarimeter which could be read and set to  $0.01^{\circ}$ . Light of wave length  $546 \mu\mu$  was used, being obtained from a mercury-vapor arc lamp and purified by a Wratten filter, No. 74.

Initial rotations were measured in samples in which the sodium carbonate was added before the invertase, which was thus rendered inactive so that no inversion took place. Identical values for the initial rotation were obtained in samples in which the aluminum hydroxide was mixed with the sugar solution before measuring out a sample of the latter and in others in which no aluminum hydroxide was used; this indicates that the volume occupied by the precipitate was negligible, and that no appreciable amount of sugar was adsorbed by it.

Solutions for the control experiments were made up with aluminum hydroxide, which was removed by filtration before the addition of the invertase. To determine whether the invertase was really adsorbed under the conditions of each experiment, a duplicate solution was prepared from which the adsorbent was filtered off about 10 or 15 minutes after the beginning of the reaction. Then a sample was taken, and the completeness of adsorption was determined by the absence of further change in rotation from that time on for a time equal to the duration of the main experiment.

In working with fairly rapid inversions, such as those in Table II, it was possible to obtain duplicate results which checked to  $0.02^{\circ}$  or better. With very dilute invertase, however, the agreement of the duplicates was worse, some differing by as much as  $0.1^{\circ}$ . This irreproducibility seems to be due to the effect of dilution noticed by Vosburgh.<sup>16</sup>

### Summary.

1. A comparison has been made of the amount of sucrose hydrolyzed in a given time by invertase combined with an adsorbent and not combined but uniformly distributed throughout the solution.

<sup>17</sup> Hudson; *THIS JOURNAL*, 30, 1564 (1908).

<sup>18</sup> Nelson and Beegle, *ibid.*, 41, 559 (1919).



2. When all conditions were the same except the presence or absence of the adsorbent and the velocity of hydrolysis was relatively large, then the amount hydrolyzed in a given time was less in the presence of the adsorbent.

3. The decrease in rate appears to be due largely to the uneven distribution of the invertase in the reaction mixture, because by preventing the settling of the adsorbent combined with the enzyme the extent of the retardation was diminished.

4. When the velocity of hydrolysis is relatively small then it is practically the same irrespective of whether the enzyme is combined with aluminum hydroxide or not. As a tentative explanation it is suggested that under these conditions the rate of diffusion of the sucrose to and the invert sugar from the enzyme combined with the adsorbent is probably greater than the rate of hydrolysis of the sucrose.

5. No evidence has been obtained so far which indicates that the true activity of the invertase, as distinguished from the resultant rate of hydrolysis of the sucrose in the mixture, is influenced by the combination of the invertase with the adsorbent.

The authors wish to express their indebtedness to the Harriman Research Laboratory, New York City, for grants in aid of this investigation.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

## DERIVATIVES OF 2,4,6-TRINITRO-BENZALDEHYDE.<sup>1</sup> II.

BY ALEXANDER LOWY AND WILMER BALDWIN.

Received June 18, 1921.

In the previous report,<sup>2</sup> the object of the research and references to the literature were given together with the theoretical phase of the subject.

The reactions investigated were all of the general type of condensations previously described<sup>3</sup> for the preparation of modified "Schiff's bases."<sup>3</sup> Condensations were carried out between 2,4,6-trinitro-benzaldehyde and the following substituted amines: *o*-anisidine, *p*-anisidine, *o*-phenetidine, *p*-phenetidine, *o*-chloro-aniline, *p*-chloro-aniline, and 2,4-dichloro-aniline.

### Experimental Part.

**Preparation of 2,4,6-Trinitro-benzaldehyde.**—The method used in the preparation of this compound was essentially that described by Sachs

<sup>1</sup> This report represents an abstract of a thesis presented by Wilmer Baldwin in partial fulfillment of the requirements for the degree of Master of Science, June, 1921.

<sup>2</sup> THIS JOURNAL, 43, 341 (1921).

<sup>3</sup> *Ber.*, 35, 984 (1902).

and Kempf and Everding.<sup>4</sup> Certain modifications of this method worked out by Lowy and Balz<sup>5</sup> in these laboratories were followed.

The table below contains an abstract of the results obtained.

Product.	M. p. ° C.	Color.	RESULTS. Crystallizing medium.	Calculated.	Found.	Calculated.	Found.
				% N.	Analysis. %.	% Cl.	%.
2,4,6-tri-nitrobenzal- <i>o</i> -phenetidine	178.5	yellow	alcohol	15.56	15.50 15.63		
2,4,6-tri-nitrobenzal- <i>p</i> -phenetidine	177	light orange	alcohol	15.56	15.60 15.45 15.30		
2,4,6-tri-nitrobenzal- <i>o</i> -anisidine	171.5	yellow	chloroform	16.19	16.04 16.10		
2,4,6-tri-nitrobenzal- <i>p</i> -anisidine	182	yellow	chloroform	16.19	16.01 16.24		
2,4,6-tri-nitrobenzal- <i>o</i> -chloro-aniline	187	yellow	acetone	15.98	15.94 15.80	10.11	10.00 9.98 9.82
2,4,6-tri-nitrobenzal- <i>p</i> -chloro-aniline	180	yellow	acetone	15.98	15.97 16.03	10.11	9.87 9.92 9.87
2,4,6-tri-nitrobenzal-2,4-dichloro-aniline	198	yellow	acetone	14.81	14.90 14.63	18.42	18.08 18.22 18.24

In the preparation of compounds listed above the ratio of one mole of 2,4,6-trinitro-benzaldehyde to one mole of the substituted amine was used in all cases. Glacial acetic acid or hot alcohol was used as condensing agent in all the above preparations. These products are soluble in acetone, chloroform and benzene and insoluble in water. On hydrolysis with 1:1 hydrochloric acid they yield 2,4,6-trinitro-benzaldehyde and the respective amines.

When the condensations of 2,4,6-trinitro-benzaldehyde and *o*-chloro-aniline, *p*-chloro-aniline, and 2,4-dichloro-aniline were carried out in hot glacial acetic acid solution, orange colored products were obtained, with melting points in all cases approximately 100° higher than those of the products prepared in the cold acetic acid solution. These compounds are insoluble in many solvents except glacial acetic acid. Preliminary work seems to indicate that they are dimolecular condensation products as exemplified by the following types. One molecule of 2,4,6-trinitro-benzaldehyde may be made to condense with 2 molecules of *tertiary* alkylated aromatic amines, substituted aromatic amines, or phenolic.

<sup>4</sup> Sachs and Kempf, *Ber.*, 35, 1236 (1902); Everding, *ibid.*, 36, 960 (1903).

<sup>5</sup> Lowy and Balz, *THIS JOURNAL*, 43, 343 (1921).

bodies to produce derivatives of triphenyl methane. Danckwortt<sup>6</sup> condensed *p*-nitrobenzaldehyde with phenolic bodies. Since these condensations present possibilities for the preparation of dyes they are now being investigated.

The above tabulated list of compounds like many other similar condensation products are affected to a considerable extent by the action of light. It was noted that the halogenated derivatives were particularly susceptible to light.

PITTSBURGH, PENNA.

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## NOTES.

**The Enzymes of the Abdominal Adipose Tissue of the Common Turkey, Meleagris Gallopavo.**—While the constants of turkey fat have been studied by several investigators, the enzymes, which occur in the adipose tissue (crude fat), have not been studied. Such a study, made upon samples of known history, is reported in this paper. The turkeys were hens, grown and killed in central Tennessee. They were marketed during the Christmas season. In trade parlance, they were dry picked, air chilled, well bled, undrawn (uneviscerated) birds. After slaughter, they were kept in a mechanically refrigerated chill room or cooler at a temperature of approximately 0° for 3 days, then were shipped to this city by express, two days being required for the journey. Upon arrival at Philadelphia, they were again placed in a mechanically refrigerated chill room, in which they were kept at a temperature of approximately 0° for from 3 to 7 days; they were then removed for study.

An aqueous extract of the abdominal adipose tissue (crude gizzard fat) was prepared as in the studies of chicken fat by Pennington and Hepburn.<sup>1</sup> The technic in the test for lipase, esterase, catalase, reductases, oxidase, and peroxidase was that used in the studies cited with the following modifications. Tributyrin was used as a substrate for lipase, and ethyl butyrate for esterase. In testing for catalase, 20 cc. of the aqueous extract was taken; and the volume of the evolved oxygen was recorded without correction. As reagents for oxidizing enzymes, use was made of  $\alpha$ -naphthol, trikresol, and phenolphthalin; when phenolphthalin was the substrate, 0.1 *N* sodium hydroxide solution was added after incubation until the phenolphthalein present showed its maximum red color.

The proper control experiments were always made on the boiled aqueous extract in order to allow for all changes in the substrate not due to enzyme action. Trikresol was used as a bactericide at a concentration of 0.2% in the tests for lipase, esterase, simple reductase, and protease.

<sup>6</sup> Danckwortt, *Ber.*, **42**, 4163 (1909).

<sup>1</sup> Pennington and Hepburn, *THIS JOURNAL*, **34**, 210 (1912); *Bur. Chemistry, Circ.*, **75**, 1 (1911); **103**, 6 (1912).

The results of the tests for *lipase*, *esterase*, *catalase*, *simple reductase*, and *aldehyde reductase* have been collected in the table; a plus + indicates the presence, a zero (0) the absence of reductase.

TABLE I.

Occurrence of Certain Enzymes in the Abdominal Adipose Tissue of the Common Turkey.

Expt. Number.	Lipase.	Esterase.	Catalase.		Reductase.	
			Cc. O <sub>2</sub> evolved.			
	Cc. 0.1 N butyric acid. Liberated in 72 hours.		30 min.	Time. 24 hours.	Simple.	Aldehyde.
Hen.						
1.....	2.20	....	12.7	39.0	+	....
2.....	5.35	1.25	10.8	....	+	0
3.....	4.90	0.35	....	7.9	+	0
4.....	6.40	0.85	....	22.5	+	Trace
5.....	6.80	0.80	....	31.4	+	Trace
6.....	4.70	0.40	....	2.0	0	0

**Oxidases** acting upon trikresol and upon  $\alpha$ -naphthol were not found. All but one of the samples contained an oxidase acting upon phenolphthalin. One sample was also tested for cresol tyrosinase,<sup>2</sup> the oxidase which produces colored compounds by its action on a mixture of *p*-cresol and amino acids or secondary protein derivatives; the substrates used were trikresol plus asparagin and trikresol plus Witte peptone; both tests were entirely negative.

**Peroxidase** acting upon  $\alpha$ -naphthol occurred in one sample, and peroxidase acting upon phenolphthalin was found in another sample. Peroxidase acting upon trikresol was not detected.

**Protease.** Two of the samples were tested for the presence of a protease. The results indicated that such an enzyme, active in the presence of hydrochloric acid, did not occur in the adipose tissue.

A 20cc. portion of the aqueous extract of one sample was permitted to act upon a flock of carmine fibrin in the presence of 0.2% hydrochloric acid; the fibrin was not attacked after incubation for 24 hours at a temperature of 37.5°.

A 2.5cc. portion of the aqueous extract of another sample was mixed with 2 cc. of a 2% solution of castor bean globulin in 5% sodium chloride solution; and 0.5 cc. of 0.1 N hydrochloric acid was then added. The precipitated protean, derived from the globulin, was not attacked during incubation for 7 days at a temperature of 37.5°.

### Summary.

Catalase, lipase (acting on tributyrin), and esterase (acting on ethyl butyrate) were always found in the adipose tissue. Simple reductase

<sup>2</sup> *Arch. sci. phys. nat.*, [4] 33, 70 (1912).

and oxidase acting upon phenolphthalin were usually present. Tests for oxidases, which act on  $\alpha$ -naphthol and on trikresol, and for protease gave negative results. Aldehyde reductase and peroxidases were found in several of the samples.

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CONTRIBUTION FROM THE CONSTANTINE HERING  
LABORATORY, HAHNEMANN MEDICAL COLLEGE  
PHILADELPHIA, PA.

Received April 23, 1921.

**Friedel and Crafts' Reaction. The Preparation of 2-*para*-Toluyyl-Benzoic Acid.**—In order to determine whether the results obtained by Rubidge and Qua<sup>1</sup> in the study of the reaction between phthalic anhydride, benzene and aluminum chloride are of general application the reaction between phthalic anhydride, toluene and aluminum chloride has been studied. In the following table the yields are calculated on the phthalic anhydride used.

No.	Toluene. G.	Phthalic anhyd. G.	AlCl <sub>3</sub> G.	Time. Hrs.	Toluyylbenz. acid. %.	Ditolyl- phthalide. %.
1	20	5	9	12	89	5.4
2	20	5	9	12	92.5	3.9
3	43	5	9	12	90	5
4	20	5	9	12	95	1.9
5	20	5	10	10	97	trace
6	20	5	4.5	12	19	34
7	20	5+5	9	12+12	19	27
8	20	5+5 cc. acet. anh.	9	12-12	none	52
9	20	5+3.2 cc. acet. anh.	9	12-12	none	45

Nos. 1 and 2 show that using the proportions of the reagents indicated the yield of toluyyl-benzoic acid is about 90%, and that some ditolyl-phthalide is formed. In No. 3 the increased amount of toluene did not materially affect the yield. In No. 4 the aluminum chloride was finely powdered and in No. 5 the slightly larger amount of aluminum chloride prevented the formation of any ditolyl-phthalide. In No. 6 with half the usual amount of aluminum chloride the yield of acid is greatly reduced and ditolyl-phthalide increased. In No. 7 the usual proportions of the reagents were used, but after 12 hours' boiling additional phthalic anhydride was added and boiling continued for 12 hours. The results show that the additional phthalic anhydride reacted with the intermediate compound to give ditolyl-phthalide. Nos. 8 and 9, with acetic anhydride used instead of the additional phthalic anhydride after the first 12 hours' boiling, gave no toluyyl-benzoic acid and a better yield of ditolyl-phthalide.

These results agree completely with those obtained by Rubidge and Qua.

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Received May 4, 1921.

<sup>1</sup> Rubidge and Qua, THIS JOURNAL, 36, 732 (1914).

## NEW BOOKS.

**The Chemical Effects of Alpha Particles and Electrons.** By SAMUEL C. LIND, Ph.D., Physical Chemist, U. S. Bureau of Mines. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 1 Madison Avenue, New York, U. S. A., 1921. 182 pp., 7 figs. 23.5 X 15.5 cm. Price \$3.00.

The first numbers of the American Chemical Society's Monograph Series will meet an inspection which will not be accorded their successors. Hence it is gratifying to see as the second of the series this able and scholarly treatise on a subject which otherwise would hardly have found a publisher.

Much in it will be new to most chemists. It deals with work which is midway between chemistry and physics, and thus has attracted only a relatively small number of investigators who are masters of both. Chemists have too generally regarded it as physics, and indeed the methods of physics are largely in evidence. Yet it is one function of that science to furnish ever new tools for the fundamental investigations of other sciences and, since the time of Lavoisier's use of the balance, chemistry has taken on new vigor with each successive adaptation of the physicist's methods. The active chemist must keep his eyes open to such possibilities, as the work of Ramsay and of Lind testifies, and as every reader who feels the inspiration of this book will admit; for we have here the application of an entirely new form of energy to the production of chemical reactions, and energy in a uniquely measurable and mechanically definite form. We are largely free from thermodynamics and statistical averages. The energy input is mechanically visible, and gives great promise of a mechanical visualization of the course of the reaction produced. The observation is intimate.

The first three chapters are devoted to an exposition of the physics involved—radioactivity and the nature of gaseous ionization. The next three record early studies of radiochemical action in gases and liquids. Then follow three chapters on the mechanism of radiochemical reactions, and in particular, the relation between gaseous ionization and chemical action, which has been the special problem of Dr. Lind himself, and which furnishes the most promising generalization in this subject, namely that for most reactions a single pair of ions corresponds to the transformation of one molecule. The exact study of the relation between ionization and consequent reactions still has a long future.

There follows an equally interesting discussion of the photochemical equivalence law. The still doubtful subject of action by positive rays and recoil atoms is discussed in Chapter XI, and the book closes with a review of Rutherford's work on the disintegration of other atoms by  $\alpha$  particles.

It should be noted that the chemical effects of electrons are hardly touched on, the vast amount of study on reactions in the various types of electron discharge being quite without the scope of this book. Indeed, the

reactions which are discussed are merely the most promising because the most intimately known of all the reactions which are produced by gaseous ionization. Chemists still need a careful analysis of the whole subject of electron effects.

Dr. Lind has given us a readable, authoritative, and complete discussion of his subject. He deserves the thanks of American chemists.

GERALD L. WENDT.

**Priestley in America, 1794-1804.** By EDGAR F. SMITH, University of Pennsylvania. P. Blakiston's Son and Company, 1012 Walnut Street, Philadelphia, Pennsylvania. 1920. i + 173 pp. 12 X 18.5 cm. Price \$2.00 Net.

On the evening of the fourth of June, 127 years ago, the 60-year old Joseph Priestley, a passenger in the good ship *Sansom*, landed in New York. Of the earlier life in England of this man, who was primarily an educator and a theologian, and not a chemist, but who, like his friend Franklin, was many-sided and had an intense curiosity regarding the secrets of nature, Thorpe has given us an adequate picture.<sup>1</sup>

In this book Dr. Smith gives us an account of the last 10 years of Priestley's life, a record of especial value not only to chemists but to all interested in the religious thought, educational ideas, and politics of this period. Contemporary letters, newspapers, and pamphlets are drawn upon largely for the story of this decade, and the excerpts throw an interesting light not only upon Priestley but upon the young republic in its experimental stage.

Priestley was warmly received on his arrival in New York as a chemist and as a leader who stood for political and religious freedom. Among the welcoming addresses was one from the Tammany Society of New York which will be to many a revelation regarding that organization. His influence was soon felt in education, and to American science the prestige of the discoverer of oxygen and the founder of pneumatic chemistry gave new impetus.

He was the friend and correspondent of Silliman of Yale, Mitchell of Columbia, McLean of Princeton, Thomas Cooper, professor of Chemistry at the University of Pennsylvania and at Carlisle, Woodhouse and the other Philadelphia chemists.

The most certain contribution to experimental chemistry from his laboratory in Northumberland was the preparation of carbon monoxide (1799), the constitution of which was clearly shown by Clément and Dé-sormes in 1801, but much of his scientific energy was spent in the defence against his American critics of his beloved phlogiston theory to which he clung to the last.

<sup>1</sup> "Joseph Priestley," T. E. Thorpe, London, 1906.

The author deals lightly with Priestley's political views. That he was a caustic critic is evident. He was out of patience with the public measures of the country. He disliked them as much as he did those of England, but added "here the excellence of the constitution provides a remedy, if the people will make use of it, and if not they deserve what they suffer."

President Adams had joined in welcoming Priestley to the new world, but they were too diametrically opposed both in religion and politics, and the friendship waned, assisted possibly by the fact that Priestley's friend Cooper was sentenced to prison in 1801 for libeling the President.

Priestley, the teacher, had many valuable ideas on education and his letters to his friend Thomas Jefferson, with whom he had much in common are decidedly interesting. They have much to do with the founding of the new college which the latter contemplated for the State of Virginia, but no inducements could win Priestley back to his early profession, and his modesty regarding his own attainments and ability as an instructor in chemistry is shown in a very candid letter refusing the professorship of Chemistry at the University of Pennsylvania.

His greatest interest was in religious matters, and he can be regarded as the first great exponent of Unitarianism in the country. By word and pen he was constantly engaged in theological discussion and exposition, a field which he regarded as his great life work. The rôle of Priestley, as a metaphysician and materialist, the exponent of a new philosophy, has been little touched upon in this volume.<sup>2</sup>

In this memoir of Joseph Priestley, Dr. Smith has made a valuable contribution to the history of chemistry in America and has fulfilled in a delightful way the wish of Harriet Martineau in her *Retrospect of Western Travel*.

"Of his retirement in America we have many particulars, but still not enough. Enough can never be learned of the course of life of one whose more homely virtues were now put to the severest test, after those which are commonly esteemed more loftily had well stood their trial."<sup>3</sup>

F. B. DAINS.

**Practical Biological Chemistry—"Guide pour les Manipulations de Chimie Biologique."**

By GABRIEL BERTRAND and PIERRE THOMAS of the Institute Pasteur. Translated from the third edition by Hector A. Colwell, M. B., D. P. H. Harcourt, Brace and Howe. New York, 1921. xxxii + 348 pp. 61 figures. 14 × 22 cm.

While the title of this volume implies its dedication to Biological Chemistry, the authors have been by no means restricted to this field. Chapters are devoted to the isolation and detection of the alkaloids, to the elements

<sup>2</sup> Prof. Woodbridge Riley ("American Thought," 1915, p. 100); "American Philosophy, The Early Schools," 1917, p. 107.

<sup>3</sup> "Retrospect of Western Travel," by Miss Martineau. p. 178.



of microbiology, glucosides, essential oils, and the description of the terpenes. Further, scattered throughout the text are a large number of directions for qualitative and quantitative procedures which, strictly speaking, fall far outside the range of Biological Chemistry.

The grouping of the subjects is widely different from that usually adopted in text-books written in English, and while the system gives the student a varied experience, there is not the same degree of logical development of the science which might result from a profound rearrangement of the subject matter. The grouping of the "Estimation of Tannin in Tanning Material" and of the "Ethereal Sulfates in the Urine" is but one illustration chosen at random. As is to be expected a relatively large amount of space is devoted to the sugars, but the quantitative methods, outside of the use of the polariscope, are confined to those suggested by the senior author. In the same way exception may be taken to the determination of such important compounds as urea, only the hypobromite method being discussed and that by means of the Bertrand method, without mention of the several other types of apparatus. The chemistry of the blood is largely ignored, that of the urine most imperfectly treated, such methods as are described being chiefly historical in interest. The newer colorimetric and nephelometric methods are not touched upon.

The translator states in his preface that the somewhat diffuse character of the subject matter is of value, as it is thus able to reach the physician, physiologist, bacteriologist, botanist, agriculturist, and those who are applying science to the furtherance of commercial enterprise. In the reviewer's opinion this constitutes a decidedly negative feature, as to cover these fields adequately means a work of far greater scope than that under consideration. Furthermore, it would mean for each of the workers listed above the necessity of searching through a considerable amount of material not germane to any of the problems arising in his special field in order to find the small amount of pertinent information.

In spite of the comparatively recent date of issue the book reminds one most strongly of those spuriously compendious treatises designed for the use of medical students in which was attempted a conspectus of the entire fields of chemistry and physics. As these encyclopedic volumes have been gradually replaced by specialized texts, so this book would seem to have been superseded by the very excellent and not over-bulky texts now available in the several fields. For the more comprehensive and exhaustive study such treatises as Abderhalden's "Biochemischen Arbeitsmethoden" are available.

In conclusion it may be said that the translation is apparently an excellent one, being clear and terse.

ALLAN WINTER ROWE.

**The Chemistry of Synthetic Drugs.** Third edition, revised. By PERCY MAY, D.Sc. (Lond.), F.I.C. Longmans, Green and Company, Fourth Avenue and 30th Street, New York, 1921. xv + 248 pp. 14 × 22.5 cm. Price, \$4.25 net.

This new edition of "The Chemistry of Synthetic Drugs" is practically identical with the second edition. It is unfortunate that in putting out a third edition, more effort has not been made to bring it up to date, by mentioning a number of substances which have excited considerable interest among chemists and which have proved of value to medical men, even though some of these substances could not yet be called large sellers from a commercial standpoint. In particular might be mentioned "Thyroxin," the trade name for the essential constituent in thyroid gland extract. Still another is "Apothesin," the hydrochloride of  $\gamma$ -diethyl-amino-propyl cinnamate, a local anesthetic used in place of procaine. It is true that this substance is inferior to procaine, but the fact that it is sold in large quantities and widely distributed makes it deserving of mention. No reference is made to benzyl benzoate or to other benzyl esters which have found such a wide and successful use in the United States as anti-spasmodics. This list could be extended to include several others of less importance which have, however, become large items in the lists of various manufacturers, such as "Oxyl-Iodide," the hydro-iodide of cincophen, "Chloroxyl," the hydrochloride of cincophen, and "Mercurochrom," the disodium salt of dibromo-hydroxy-mercury-fluorescein. All of these substances are synthetics which have attracted more especial attention in the United States during the last three years. Undoubtedly others of real and permanent importance have been discovered and marketed in European countries, but a knowledge of them has not yet become general in this country.

The new points in this edition are a page devoted to a description of "eccaine," a new local anesthetic of complex nature made from certain decomposition products of cocaine, and a few additional sentences of which one concerning mustard gas and a second concerning trinitrotoluene may be mentioned.

For those who are not acquainted with this book by Percy May, it may be said that it presents in a concise and readable form the fundamental facts about the majority of important synthetic drugs and extracted substances which have proved valuable in the medical profession. Methods of preparation are discussed and uses noted. The book may be highly recommended to any one who wishes to acquire a general knowledge of this field.

ROGER ADAMS.

**Organic Medicinal Chemicals (Synthetic and Natural).** By M. BARROWCLIFF and FRANCIS H. CARR. Industrial Chemistry Series, edited by Samuel Rideal. D. Van Nostrand Company, 8 Warren Street, New York, N. Y. 1920. xiii + 331 pp., 24 figures. 14 × 22 cm. Price, \$4.00.

This volume deals with a phase of the chemistry of medicinal drugs

which has never before been emphasized and will be very useful to organic chemists and to pharmacologists who desire to know how the substances which he uses are produced on a large scale. The authors deal very briefly indeed with the pharmacological action of the substances considered and the book is in no sense a text-book of pharmacology. However, the pharmacological statements are in the main sufficiently accurate. The writers discuss briefly in connection with each type of drug the relation of chemical constitution to pharmacological action. The main emphasis is placed upon the methods of large scale production, and the text contains many figures illustrating the types of apparatus used. The book should tend to stimulate the interest of the organic chemists in the synthesis of medicinal substances and also interest of students in the methods used in the large scale production of organic medicinal drugs.

A. S. LOEVENHART.

**Chemistry Review Book—Including Recent Examination Questions.** By M. H. KESSEL, B.S., Science Master in the Clark School for Concentration, New York City. Globe Book Company, New York, 1921. 96 pp. 16 figures. 15.5 × 23 cm. Price, \$0.67.

This little book is a careful compilation of definitions, equations, and laws together with very brief statements in regard to properties, uses, and processes which the student is most likely to need in preparing for an examination in chemistry. In this field the book will probably serve a useful purpose. It is the best of its kind that we have seen.

N. HENRY BLACK.



# THE JOURNAL

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### American Chemical Journal

(Founded by Ira Remsen)

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY.]

#### THE CATALYTIC OXIDATION OF CARBON MONOXIDE.<sup>1</sup>

By T. H. ROGERS, C. S. PIGGOT, W. H. BÄHLKE AND J. M. JENNINGS.

Received July 12, 1920.

#### Introduction.

This problem was a phase of the War Gas Investigations and was undertaken at this laboratory<sup>2</sup> early in May 1917, under the auspices of the U. S. Bureau of Mines, with the object of providing a mask ingredient which would afford protection against carbon monoxide when present in air. The desired application and the necessary specifications of such a material having been described<sup>3</sup> in detail, the present article presents, from the chemical standpoint, the most important features of the development of a suitable oxidizing catalyst.

#### General Statement.

† work was done in making comparative tests of the materials of the literature as capable of oxidizing carbon monoxide at various pressures,<sup>4</sup> always with the object in view of ultimately making a selection, by permission of the Director of the Chemical Warfare Service. The investigation was directed by Professor J. C. W. Frazer, who is one of the authors of the general article, Lamb, Bray and Frazer, *J. Ind. and Eng. Chem.*, 12, 1920, concerning the treatment of this problem as a whole by various laboratories with the Central Laboratory at Washington. See also Frazer, *ibid.*, 13, 1921, and Frazer, Ref. 2. See also von Kralitz, "Handbuch d. anorganischen Chemie," on carbon monoxide.

the reaction catalytic. It was observed while doing this preliminary work that many of these substances when intimately mixed gave a material much more active than any one of its constituents. For example, while neither chromium trioxide,  $\text{CrO}_3$ , nor yellow mercuric oxide oxidized carbon monoxide appreciably when a low concentration of this gas in air was passed through a tube containing these materials, a mixture of the oxides containing chromium trioxide, in excess of equivalent proportions was found to possess considerable oxidizing power and about 50% of the carbon monoxide was oxidized for a short period.

Again, silver oxide which oxidizes carbon monoxide only slowly at room temperatures, when mixed in various proportions with calcium hydroxide showed markedly greater activity, evidencing the increased activity of mixtures over that of single constituents. Other important factors, more or less self-evident, in the use of mixtures of two or more substances are the fineness of subdivision and intimate admixture of these substances, the resulting product being essentially a solid solution in certain cases. When a mixture of silver and calcium hydroxides was prepared by the simultaneous precipitation of the hydroxides from a water solution of the nitrates of these metals, and the precipitate washed and dried at  $120\text{--}130^\circ$  in a current of oxygen a material was obtained having marked activity. When dried in a current of air or oxygen the color of this mixture at times changed during the process of drying from a light brown to a slate color, a color change which indicates the decomposition of the silver oxide. On examination it was found that globules of metallic silver could be seen in the material. This decomposition was observed at  $100^\circ$  in the air and at  $130^\circ$  in oxygen, whereas the decomposition pressure of silver oxide is but 0.2 atmospheres at  $130^\circ$ . This notable increase in the decomposition pressure of silver oxide is being investigated further to determine whether the phenomenon is due to fineness of subdivision or to some other cause connected with the presence of calcium hydroxide, one effect of which may be to prevent the increase in size of the silver oxide particles.

The activity of these mixtures of silver oxide and calcium hydroxide was slightly increased by the addition of a small quantity of sodium hydroxide. The oxidation of the resulting material (about 80% for 20 min) was entirely due to the combined oxygen, as the amount of oxygen consumed was never more than could be accounted for by the silver oxide.

Manganese dioxide was ultimately found to be an essential part of the best catalysts, and here also the same general statement may be applied. Mixtures of manganese dioxide and silver or calcium hydroxide were found to be much more active towards carbon monoxide than the oxides used separately. The addition of a third component, sodium hydroxide, was advantageous in the preliminary experiments. The action of these mixtures containing sodium hydroxide was

not catalytic. They functioned for only about 40 minutes under the testing conditions given below and the amount of oxidation was not greater than could be accounted for by the active oxygen contained in the material. The behavior of these mixtures is shown in Table I.

It was not until finely divided manganese dioxide was prepared, and special precautions, listed later, were used to secure the admixture therewith of other oxides, that the catalytic oxidation of carbon monoxide at room temperature was satisfactorily solved. The most satisfactory catalysts were obtained by using a mixture containing either silver oxide or copper oxide and manganese dioxide. Of these mixtures those containing silver oxide seemed to be more active than those containing copper oxide. Other oxides such as iron oxide may be tolerated in certain amounts in the final products, but such oxides seem to act more as inert diluents and decrease rather than increase the activity of the material. However, when catalysts are prepared by properly mixing manganese dioxide with both silver and copper oxides such catalysts may be quite as active as those containing either copper or silver oxide alone.

The conclusions reached from the preliminary work on manganese dioxide were, first, that the degree of subdivision was an extremely important factor in the activity of this material; and, second, that the activity is also greatly increased by properly incorporating with finely divided manganese dioxide, other metallic oxides such as copper and silver oxides.

A comparative study was then made of samples of manganese dioxide prepared by the following methods.

1. **Reduction of Potassium Permanganate by Methyl Alcohol.** (a)—When a warm solution was reduced, the manganese dioxide particles were comparatively coarse, settling rapidly, and the mixtures prepared from such materials were not very active (Table I (a)). When the reduction was brought about in a cold solution a more flocculent precipitate was obtained which settled more slowly than (a), and it will be seen by referring to Table I that the silver oxide mixtures were more active than similar mixtures made from samples (a).

The mixtures of silver oxide and manganese dioxide made from both (a) and (b) above were quite efficient in bringing about the oxidation of carbon monoxide for an hour or more and the oxygen consumed was greater than the available oxygen of the material, showing these samples to be partially catalytic. The active zone of the material at any time during the test could be immediately ascertained by the location of the warm portion of the tube. This zone moved along gradually as the efficiency of that portion dropped and finally passed to the bottom of the tube, when carbon monoxide could be detected in the effluent gas. Prior to this, however, the action was 100 % efficient.

2. **The Frémy Method.**<sup>5</sup>—One hundred g. of finely ground potassium permanganate is added to 500 g. of conc. sulfuric acid in 150 cc. of water, cooled, carefully stirred, and allowed to stand, when the permanganic acid formed decomposes, giving off oxygen. Permanganic anhydride,  $Mn_2O_7$ , will sometimes separate as an oil which is extremely

<sup>5</sup> Frémy, *Compt. rend.*, 82, 1213 (1876). We are indebted to W. A. Patrick for suggesting this method of preparation.

explosive. When all the permanganic acid is decomposed the manganese dioxide is washed in a large quantity of water by decantation until free from sulfates. At the final washing the precipitate approaches the colloidal condition and settles very slowly. The manganese dioxide still contains a small quantity of a potassium salt, which is evidently very strongly adsorbed. The oxide mixtures prepared from this grade of manganese dioxide were truly catalytic, and, when tested on dry gas, showed that a layer only about 1 cm. deep was entirely efficient in oxidizing carbon monoxide. This method of preparation of manganese dioxide was generally used in the work of development of the optimum proportions of the constituents.

**3. Electrolytic Method.**<sup>6</sup>—This consists in the electrolytic oxidation of manganese in an ammonium carbonate solution using a ferromanganese alloy as the anode. The ammonium permanganate formed decomposes with the precipitation of finely divided manganese dioxide. When a 2-component cell is used this decomposition takes place best at temperatures slightly above 40°. When a 1-compartment cell is used oxidation and reduction take place simultaneously, thus permitting lower temperatures and consequently finer manganese dioxide. The material so produced was not uniform but the best preparations were very active.

**4. Reduction of Permanganic Acid by Oxalic Acid.**—Permanganic acid, prepared from the calcium salt is diluted with a considerable quantity of water, well cooled and a cold solution of oxalic acid is added in slight excess. As carbon dioxide is the by-product, no washing is necessary. This manganese dioxide with silver oxide produced a catalytic material of unlimited life.

**5. Decomposition of Ammonium Permanganate.**—One hundred g. of calcium permanganate is dissolved in 500 cc. of water, and ammonium carbonate solution containing a little ammonia is added. Calcium carbonate is filtered off, and the ammonium permanganate, diluted to 4 liters, is reduced slowly in the cold with methyl alcohol. This method gives very finely divided manganese dioxide and yields uniformly active catalysts of unlimited life. It is probably superior to that prepared by Method 1, because ammonium salts are less strongly adsorbed than are potassium salts.

**6. Air Oxidation of Manganese Oxide.**—The probable mechanism of catalytic oxidation by manganese dioxide, *viz.*, oxidation and reduction of the oxides of manganese, indicated that a catalyst might be prepared from manganous hydroxide and its oxidation effected before use, by drying in atmospheric oxygen. Manganous and silver oxides, precipitated simultaneously from a solution of the nitrates, were dried in oxygen at 130°; a number of mixtures of moderate life were thus produced, but the product was not of uniform activity. Results using copper oxide were less encouraging.

**Preparation of Catalytic Material.**—The oxide catalysts were prepared by the following method, which was used quite generally throughout the investigation whenever the solubilities of the salts used permitted. Manganese dioxide paste of known water content (60–65%) was weighed and suspended in a large volume of cold water, care being taken to secure a uniform suspension; to this was added a standard silver nitrate solution sufficient to give the desired amount of silver oxide in the final mixture. After thorough mixing silver hydroxide was precipitated by a slight excess of sodium hydroxide solution, with constant stirring. After filtering and washing free from sodium nitrate, the mixture was dried on a water-bath and then at about 125° in air or, preferably, in dry oxygen. The drying

<sup>6</sup> This method was developed by B. F. Lovelace.



must be quite thorough, otherwise the mixture will not function catalytically.

Copper oxide cannot be incorporated with manganese dioxide by the above method and a good catalyst obtained, but by using the method of precipitating with a sodium carbonate solution as described below an excellent catalyst may be made containing only manganese dioxide and copper oxide.

An important variation of the above method consisted in the precipitation of silver (or copper) as carbonate, rather than the oxide. During the subsequent drying the carbonate hydrolyzed almost completely, so that what was essentially the oxide mixture was finally produced, similar to the above but more active, especially in the case of mixtures containing only copper oxide and manganese dioxide. When 3 component mixtures were prepared (silver oxide, manganese dioxide and cupric oxide) the nitrates of copper and silver were added to the suspension of manganese dioxide.

It has been stated that Methods 2, 4 and 5 produce the most suitable manganese dioxide for a catalytic material when mixed with other oxides. The relative activities of the different samples were better shown when the amount of silver oxide in the material was reduced (Table III). The most effective mixture prepared according to Method b contained 62.5% of silver oxide, while with that made by Methods 2, 4 and 5 the silver oxide content was successfully reduced to 37.5%, and to 28% when the silver was precipitated as carbonate. The 3-component mixtures (silver oxide, cupric oxide and manganese dioxide), described above, were developed with a practical end in view, *i. e.*, to reduce the cost of the catalyst. In this connection the precipitation as carbonates was especially valuable and, as stated above, the silver oxide could then be completely replaced by cupric oxide when using manganese dioxide prepared by the Frémy method.

Special tests on the most active 2-component catalyst (62.5% of manganese dioxide, 37.5% of silver oxide) are of interest. After a 10-hour test on 1% carbon monoxide with 100% efficiency, the material was allowed to cool and a 0.3% carbon monoxide mixture run in at the same rate (500 cc./min.). The warm area (about 0.5 cm. in length) immediately reappeared at the same place and remained stationary for 10 hours longer, no carbon monoxide at all being detected in the effluent gases at the end of this time. The "pick up" of the catalyst was excellent; as the material was found to function at even lower than room temperature, there was no initial period of low efficiency while the catalyst was warming up.

#### Effect of Humidity.

Inasmuch as these catalysts were to be used for military and naval purposes under all weather conditions with varying temperatures

and humidities, the effect of these factors was of considerable importance.

At low temperatures a poor catalyst was less active, but a good catalyst would give 100% efficiency immediately, under varying concentrations of carbon monoxide at all temperatures covered in any tests,  $-5.0^{\circ}$  being the lowest temperature used. The greater the concentration of carbon monoxide (the rate of flow being the same) the more the catalyst would automatically heat up. The most active catalysts were exposed to both high (2% to 5%) and low (0.08% to 0.1%) concentrations of carbon monoxide at temperatures ranging from  $+100^{\circ}$  to  $-5^{\circ}$  without any detectable loss of efficiency.

With water vapor the case was quite different. As has been indicated above, the deleterious effect of moisture was recognized early in the investigations while working out the best conditions of drying the first catalysts produced. Samples which were not entirely dry possessed little or no activity, while a good dry sample broke down when exposed to any appreciable quantity of water vapor. However, a catalyst which had been rendered inactive in this way could be "regenerated" by drying at  $130^{\circ}$  in a stream of dry air or oxygen. From the military point of view this effect of moisture was of great importance and efforts were made to combat it. This effect of water vapor is a necessary result of the fine structure of the catalyst, and is obviously due to condensation in the pores of the material.

The ordinary mixture is rather soft and very porous and has a low apparent density. However, if this material be put in a press while still moist and subjected to a high pressure (2819 kilograms per sq. cm.) the apparent density is greatly increased and the resultant cake when dried, is relatively hard and quite resistant to crumbling, which in itself is of great importance in the military canister. A material so treated is more resistant to moisture and will last longer than the same volume of the unpressed material against a gas mixture of a given humidity. Tests were made on both pressed and unpressed catalysts at relative humidities from 25% to 100%, the pressed material in each case having a somewhat longer life.

#### Methods of Testing and Analysis.

The standard test prescribed by the Bureau of Mines was used throughout, except in special cases. This consisted in passing the air-gas mixture at the rate of 500 cc. per sq. cm. of cross section per minute through a layer of the catalyst 10 cm. deep. This corresponds to a rate of 32 liters per minute for a canister of regulation size, and is about twice the average rate of breathing.

The standard concentration was 1.0%, regulated by mixing pure carbon monoxide and air in the proper proportion through flow meters. For the catalyst, glass tubes were used having 1 sq. cm. cross sectional area, the granular material to be tested being poured in and the tube gently tapped to cause moderate settling.

The catalyst before being tested was broken up and screened and that portion which passed through the 10-mesh sieve and was retained by the 20-mesh was used. Conditions in a canister are more favorable than those of the tube test, since in a layer of broad cross sectional area there is less channeling of the gases and the loss of heat by radiation is less.

Samples, 500 cc. in volume, of the gases issuing from the test-tubes, were taken in glass bottles by displacement of water. A sample was taken immediately after the run was started and at regular intervals (usually 10 minutes) thereafter. These samples were analyzed by the iodine pentoxide method, consisting of passing the gases over a considerable quantity of pure iodine pentoxide at 160°. The gases from the sample bottle were passed successively through standard barium hydroxide, over calcium chloride, iodine pentoxide, and finally through potassium iodide solution and then through barium hydroxide. The barium hydroxide was titrated with standard oxalic acid, and in this way the quantity of carbon monoxide oxidized by the catalyst and that oxidized by the iodine pentoxide was determined, thus furnishing a check on the analysis. This method of analysis is quite accurate and, by using a large quantity of iodine pentoxide can be made with reasonable rapidity. Frequent analyses of the gases passing effluent to the flow meters were made as a check on the flow meters.

TABLE I.  
EFFECT OF ADDITION OF SODIUM HYDROXIDE TO  $\text{MnO}_2\text{-Ag}_2\text{O}$  MIXTURES.  
Rate: 500 cc./min. 1.0% CO.  $\text{MnO}_2$  made by Method I a.

$\text{MnO}_2$ , %.	$\text{Ag}_2\text{O}$ , %.	$\text{NaOH}$ , %.	%	%	Percentage efficiency, Time in minutes.			
					%. %	%. %	%. %	%. %
27.8	69.4	2.8	100	98	88	40	10	..
27.0	67.6	5.4	100	100	92	38	22	..
26.3	65.6	7.9	100	100	99	98	63	..
25.6	64.1	10.3	100	100	100	100	88	..
25.0	62.5	12.5	100	100	100	100	100	98
25.0	62.5	12.5	100	100	100	99.5	95.6	..
25.0	62.5	12.5	100	100	98	90.1	88.5	..

TABLE II.  
RELATION OF DEGREE OF SUBDIVISION TO CATALYTIC LIFE.  
Rate: 500 cc./cm.<sup>2</sup>/min. 1.0% CO.

$\text{MnO}_2$ , %.	$\text{Ag}_2\text{O}$ , %.	Type of $\text{MnO}_2$ .	Catalytic life, % efficiency.
50	50	1 a	98%, end of one hour; 10%, end 2 hrs.
50	50	1 b	97%, end of one hour; 60%, end 2 hrs.
50	50	6	Limited life
55	45	6	100%, end of 5 hrs; limited life
50	50	2	Catalytic; unlimited life
50	50	5	Catalytic; unlimited life
50	50	4	Catalytic; unlimited life

TABLE III.  
MANGANESE DIOXIDE AND OTHER OXIDES.

Type of $\text{MnO}_2$ .	$\text{MnO}_2$ , %.	$\text{Ag}_2\text{O}$ , %.	$\text{CuO}$ , %.	$\text{Co}_2\text{O}_3$ , %.	Remarks.
2	62.5	37.5	10.0	..	Unlimited; 7 hours
4	72.0	18.0	..	..	No activity
2	50.0	40.0	10.0	..	Unlimited life
2	50.0	30.0	20.0	..	Unlimited life
2	50.0	20.0	30.0	..	Unlimited life

TABLE III (*continued*).

Type of MnO <sub>2</sub> .	MnO <sub>2</sub> , %.	Ag <sub>2</sub> O, %.	CuO, %.	Co <sub>2</sub> O <sub>3</sub> , %.	Remarks.
2	50.0	10.0	40.0	..	100%, 6 hours
1 a	20.0	40.0	..	40.0	94%, 80 min.
1 b	20.0	40.0	..	40.0	100%, 80 min.
2	50.0	..	..	50.0	100%, 20 min.
2	50.0	25.0	..	25.0	Unlimited life
6	72.0	18.0	..	..	Slight activity
6	62.5	..	37.5	..	No activity
6	66.6	13.4	20.0	..	100%, 5 hours

TABLE IV.

## MANGANESE DIOXIDE AND OXIDES PRECIPITATED AS CARBONATES.

Type of MnO <sub>2</sub> .	MnO <sub>2</sub> , %.	Ag <sub>2</sub> O, %.	CuO, %.	Remarks.
2	83.2	16.8	..	No activity
5	77.3	22.7	..	100%, 4 hours; limited
5	70.1	29.9	..	Catalytic; unlimited
2	70.0	30.0	..	Catalytic; unlimited
2	60.8	..	39.2	100%, 5 hours
2	80.4	..	19.6	95%, 8 hours
2	71.4	..	28.6	Catalytic
2	54.8	5.4	39.1	Catalytic
2	68.4	6.8	24.8	100%, 8 hours; limited life

## Discussion.

The present investigation relates entirely to experiments which were made for the purpose of affording protection against the poisonous action of carbon monoxide. It was done under the stress of war conditions when no opportunity was afforded to investigate the mechanism of the reactions involved. The physical structure of the oxides in the catalysts described is an essential factor in their activity; this matter is now being investigated by a careful study of their adsorption isotherms. However, certain facts were noted in the course of this work which appear to have relation to a possible chemical explanation of the reaction. The fundamental assumption of such an explanation is that the oxygen used for the oxidation of the carbon monoxide comes immediately from the oxide catalyst, and that in turn the catalyst is reoxidized by the oxygen of the air sufficiently rapidly to maintain its oxygen content and high activity. As the catalysts are mixtures of more than one oxide it is a question which of these plays the principal rôle. Since both silver oxide and manganese dioxide as prepared above will oxidize carbon monoxide at room temperature, either may be considered as the initial cause of the reaction. But both of these oxides when used alone suffer loss of oxygen, soon lose their activity and are not catalytic in their action. Copper oxide does not oxidize carbon monoxide at an appreciable rate at room temperatures. As the catalysts described above all contain manganese dioxide as an essential constituent, and as the physical condition of the manganese dioxide is of paramount importance it

is assumed on the basis of the above facts that the manganese dioxide is the initial cause of the oxidation, probably functioning by reason of the variable valence of the manganese. Manganese dioxide prepared by any method yielding relatively coarse particles has very slight activity, whereas if its particles are practically of colloidal dimensions it uniformly produces a satisfactory catalyst. Fine subdivision of the particles of the other constituents and their intimate contact with the manganese dioxide particles tend of course toward the production of the most reactive material. On the basis of this explanation of the reaction, the single oxides are not reoxidized by oxygen fast enough to maintain catalytic action; the function of the other oxide or oxides is to increase the velocity of reoxidation of the manganese dioxide, and for this purpose silver oxide appears to be more efficient than copper oxide. In support of this view is the fact that a material prepared by simultaneous precipitation of manganous and silver hydroxides can be made very reactive by air oxidation at 125°. Of course the alternative is to assume that silver or copper oxide is the immediate cause of the action and that manganese dioxide catalyses the reoxidation of the reduced oxides. In favor of this assumption is the fact that manganese dioxide is a good catalyst for the decomposition of such metallic oxides as those of silver and mercury. The present work furnishes no proof of either view, and until further observations on the behavior of these oxide mixtures are available both views are tentative.

Another fact related to the intermediate oxide theory is that a mixture which is partially catalytic, as is the case when the catalyst is not sufficiently active or when the catalyst is poisoned by water vapor, always loses "available" oxygen. The first explanation of the poisonous effect of water vapor would be that the loss of activity results from a diminution of the large internal surface, so essential in these catalysts, which is in part covered by liquid water. This, however, seems hardly to account for all the facts, since under these conditions the catalyst suffers reduction, therefore the carbon monoxide in the mixture has access to the catalyst. The loss of activity seems to result, therefore, primarily from the inability of the catalyst surface to recombine with oxygen. It is possible that this is due to a condensation of water within the pores of the catalyst which thereby separates the oxide particles and thus prevents the intimate contact of the oxides which is essential for the catalytic activity of the material. Some of these points are under investigation, and it is realized that a further discussion is premature until these results, especially those bearing on the adsorption of these catalysts, are available.

The use of these oxides as catalysts is naturally not limited to carbon monoxide, but may be applied to a number of other substances; further work along these lines is in progress, including the oxidation of ammonia. The range of applicability is quite wide, especially in the field of organic oxidations, depending of course, on the possibility of carrying out the

reaction in the vapor phase. It has been found that the action is too energetic in some cases, but the possible variations in physical properties and in constituents present many possibilities, as is illustrated by the varying degrees of activity toward carbon monoxide observed in the various mixtures during the present investigation. Thus the degree of catalytic activity may be adapted and controlled to suit the conditions of each oxidation reaction.

### Summary.

1. The decomposition temperature of silver oxide when simultaneously precipitated with calcium hydroxide is considerably lower than that of silver oxide alone.

2. A number of catalysts have been prepared which cause rapid and complete oxidation, at ordinary temperatures, of carbon monoxide in any concentration at which sufficient oxygen is present.

3. The essential constituent of this class of catalysts is specially prepared manganese dioxide, upon which is precipitated the oxide of silver or copper or both.

4. The silver or copper is best precipitated as the carbonate, and subsequently hydrolyzed to the oxide.

5. The presence of water vapor limits the life of these catalysts.

6. The application of this class of catalysts to a number of oxidation reactions is suggested.

In conclusion the authors desire to pay full tribute to Professor Frazer, to whom principally the success of this investigation is due, whose resource and pertinacity were a source of inspiration to those associated with him.

BALTIMORE, MARYLAND.

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[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE.<sup>1</sup>]

## THE CATALYTIC OXIDATION OF CARBON MONOXIDE AT ORDINARY TEMPERATURES.

BY DAVID R. MERRILL AND CHARLES C. SCALIONE.

Received March 2, 1921.

The experimental work upon which this paper is based was done by the authors and their associates largely for the purpose of developing a suitable absorbent for carbon monoxide for use in gas masks,<sup>2</sup> and, because of the importance of obtaining production on a large scale without delay, it was not possible to investigate the scientific aspects of the problem as thoroughly as could be desired. An endeavor has been made in the preparation of the present paper to choose, from the large mass of data obtained,

<sup>1</sup> Published with the permission of General Amos A. Fries, Chief of the Chemical Warfare Service.

<sup>2</sup> An historical review of the investigations connected with the problem of the carbon monoxide mask giving due credit to the various persons concerned has been published by A. B. Lamb, W. C. Bray and J. C. W. Frazer in the *J. Ind. Eng. Chem.*, 12, 213 (1920).

such typical data as are of scientific interest, and to present them for the use of other investigators in this field.

It is well known that, in spite of the large decrease in free energy in the oxidation of carbon monoxide by atmospheric oxygen, the rate of this reaction at room temperature is entirely negligible in the absence of catalysts. The activity of platinum and palladium blacks in catalyzing this reaction has long been recognized, but no examples of active catalysts containing only the more common metals were found in the literature at the time the present investigation was begun. The work of Wright and Luff<sup>3</sup> on the minimum temperature of reaction of carbon monoxide with various metallic oxides had indicated the possibility of preparing oxides of sufficient activity<sup>4</sup> for use as oxidizing agents in carbon monoxide masks, although these investigators did not conduct their experiments in such a way as to show whether or not the oxidation would be catalytic in the presence of excess of oxygen.

The present investigation was undertaken in an endeavor, by suitable variation of the chemical composition and physical properties of mixtures of metallic oxides, to prepare a solid substance which would oxidize dilute carbon monoxide—air mixtures with reasonable completeness at ordinary temperatures and fairly high rates of flow. These properties are of course more essential in a practical absorbent than is catalytic activity. Because of the desirability of the latter, however, the choice of materials for experimentation was based both on the suggestions obtained from the work of Wright and Luff and on the chemical theory of catalysis. According to this theory the catalyst actually takes part in the reaction, oxidizing the carbon monoxide and being itself reoxidized by the oxygen of the air. In order that this may take place it is necessary that the oxide be readily reduced and also that in its lower state of oxidation it be readily oxidized. Suitable couples of higher and lower oxide or oxide and metal are more likely to be found where more than one oxide of the metal is known than where the metal is readily oxidized to a single oxide. By the application of these ideas, it was found possible to prepare oxide mixtures (called for convenience Hopcalite or HC<sup>5</sup>), which catalyze the oxidation of dilute carbon monoxide—air mixtures at ordinary temperatures<sup>6</sup> for

<sup>3</sup> C. R. A. Wright and A. P. Luff, *J. Chem. Soc.*, 33, 1, 504 (1878); cf. Fay, Southerland and Lane, *Polytech. Eng.*, 10, 72 (1910).

<sup>4</sup> Lamb, Bray and Frazer, *Ref. 2*, p. 214.

<sup>5</sup> J. C. W. Frazer and C. C. Scalione, U. S. pat. 1,345,323, June 29, 1920. *C. A.*, 14, 2533 (1920).

<sup>6</sup> Rideal and Taylor (*Analyst*, 44, 89–94 (1919), *C. A.*, 13, 1169 (1919)) have applied metallic oxides to the preferential oxidation of carbon monoxide in hydrogen, but their catalysts apparently are not sufficiently active to oxidize carbon monoxide at room temperature. Cf. Harger and Terrey, Brit. Pat. 127,609, Apr. 28, 1917. *J. Soc. Chem. Ind.*, 38, 577A (1919).

an indefinite length of time when protected from moisture, as by a layer of calcium chloride in the canister.

### General Description of the Catalysts.

An absorbent, to be suitable for use in gas-masks, must have a very high activity in proportion to its volume.<sup>4</sup> Since, in heterogeneous catalysis, the amount of reaction that a catalyst is able to bring about is a function of the surface exposed, it was important to prepare the catalysts in a form exposing the maximum surface, and this was accomplished by preparing the oxide mixtures in the form of porous granules. The use of ignited oxides was not satisfactory because of their low activity at ordinary temperatures. Precipitated oxides were found to be more active, but granules prepared by simple drying and crushing of the filter cake were often lacking in mechanical strength; and no binders were found that did not materially reduce the activity of the resulting product. It was found, however, that fairly hard granules could be obtained by careful control of the conditions of precipitation, and that the hardness could be further increased by submitting the filtered precipitate to high pressure in a hydraulic press before drying.

Among the various oxides and mixtures investigated there were two mixtures which were particularly active, and it was these which were studied in most detail. The first will be referred to as the 4-component mixture (or Hopcalite I) and consisted of approximately 50%  $\text{MnO}_2$ , 30 %  $\text{CuO}$ , 15 %  $\text{Co}_2\text{O}_3$  and 5 %  $\text{Ag}_2\text{O}$ . About 7,300 kg. of this mixture was produced on the large scale and used to fill about 40,000 canisters.<sup>7</sup> The second mixture, referred to as the 2-component mixture, consisted ordinarily of 60 %  $\text{MnO}_2$  and 40 %  $\text{CuO}$ , and, although somewhat cheaper, was developed too late for use on the large scale.

For use in gas masks, the granules were screened between 8- and 14-mesh screens, as this range of sizes gave a suitable balance between excessive pressure drops from fine granules on the one hand, and poor efficiencies due to channeling and mechanical leakage with thin layers of comparatively coarse granules on the other. The color of the granules of either mixture is a brownish black, and most samples are abraded somewhat more readily than the army soda-lime. An investigation made by G. A. Hulett of the porosity of a sample of 4-component mixture, 14-16 mesh, gave the results indicated below. The apparent density of the granules was 0.501 g. per cc. The true density of the solids was determined from the actual volume displaced, after evacuation under water to displace the air in the capillaries by water, and was found to be 5.65 g. per cc. The granules were then centrifuged to remove the excess water but leave that filling the capillaries. This latter was determined from the

<sup>7</sup> Lamb, Bray and Frazer, Ref. 2, p. 220.



increase over the original dry weight, and amounted to 88 cc. per 100 g. This is equivalent to 8.8 cc. of solids, 44.2 cc. of capillary voids and 47 cc. of gross voids per 100 cc. of granules. This is a high degree of porosity<sup>8</sup> and results in the catalysts being excellent absorbents for organic compounds of high molecular weight such as some of the war "gases."

**Factors Influencing Activity.**—The factors influencing the activity will be discussed in detail in connection with the preparation of the individual oxides, but it may be said that in general the activity of the mixtures is dependent upon the preparation of the individual oxides in a high state of oxidation and a suitable physical condition. The complexity of the problem of determining the effects of the various factors may be judged from the number of variables which must be considered. The more important of these are as follows: the choice of the constituents of mixtures of oxides and the methods of preparation of the individual oxides; the completeness of washing of the precipitates; the methods of mixing and filtration; the kneading and high-pressure filtration or other treatment of the wet cake; the conditions of drying and final moisture content; and the size of granules and method of utilization of fines. The activity is also dependent upon the conditions of test, such as the temperature, moisture content, concentration and rate of flow of the gas.

**Methods Used in Testing the Catalysts.**—The activity of the catalysts at room temperature was determined by the use of apparatus of the same general design as that used in testing other absorbent materials for use in gas masks. The glass tube containing the sample had a cross sectional area of about 1.5 sq. cm. and the normal depth of layer used was 5 cm. Free radiation was permitted from the tube and most of the tests were made with a room temperature of 25°. The carbon monoxide was prepared either by the action of sulfuric acid on formic acid or by the reduction of carbon dioxide by charcoal in a tube furnace. The standard rate of flow of the carbon monoxide—air mixture through the absorbent was 500 cc. per minute per sq. cm. of gross area, which, with a depth of layer of 5 cm. is equivalent to a space velocity of 6000 cc. of gas mixture per hour per cc. of catalyst. Most of the tests were made using a 1% mixture although some were made with 0.15 % or 0.25 % to determine whether the reaction would start properly with such dilute gas. The influent gas was analyzed occasionally and the effluent gas continuously by means of the Lamb and Larson calorimetric device<sup>9</sup> which was found very convenient for the purpose. The device was calibrated frequently by comparison with analyses by the iodine pentoxide method.

<sup>8</sup> For data on the porosity of charcoal, cf. H. E. Cude and G. A. Hulett, *THIS JOURNAL*, **42**, 391-401 (1920) and H. H. Lowry and G. A. Hulett, *ibid.*, **42**, 1393-1408 (1920).

<sup>9</sup> A. B. Lamb and A. T. Larson, *THIS JOURNAL*, **41**, 1908 (1919).

For the tests with dry gas, the mixture was passed through two bead towers, into which conc. sulfuric acid dripped. For the tests with humidity another pair of towers was used and dil. sulfuric acid of the proper concentration to give the required vapor pressure of water. The activity specifications for the material prepared on the large scale have been already recorded.<sup>7</sup>

The apparent density of the granules was determined from the weight of 50 cc. measured in a special tube which permitted a standard degree of packing to be obtained. The hardness or resistance to abrasion the granules was determined by a method similar to that used for soda-lime. This consisted in shaking a weighed amount of the granules with steel balls in a pan on a Rotap machine for a definite length of time, removing the balls and weighing the granules retained on a 20-mesh screen. The percentage retained was called the hardness number. The time of shaking was chosen so as to give numbers between 50 and 80 for the majority of samples, as the results were more reproducible within this range. The values so obtained are only relative and cannot be compared directly with those for the somewhat harder army soda-lime where the standard time of shaking was longer.

#### **Standard Methods of Preparation of the Oxides and Mixtures.—**

As a guide to those who may wish to prepare these catalysts for experimental purposes, the methods used in their preparation on the small scale will be given in detail. On the large scale the methods were essentially the same except in the case of the manganese dioxide. With this oxide it was difficult to reproduce small-scale conditions, and some variations were therefore necessary in adapting the process to large-scale production. The methods used in the preparation of the 4-component mixture will be described first.

*Preparation of Manganese Dioxide.*—One hundred and fifty g. of finely ground anhydrous manganese sulfate is mixed rapidly with 142 g. of water in a container arranged for cooling and thorough mechanical agitation. Without further delay 675 g. of 93% sulfuric acid is added with constant agitation. This produces a fine suspension of manganese sulfate in about 77 % sulfuric acid. As soon as the temperature falls to 50°, 150 g. of potassium permanganate is added in small portions at a time in the form of a coarse powder. The addition should take 15 to 20 minutes and the temperature should not rise above 75°. After about 10 minutes more at 60° the reaction is practically complete and the mixture is poured in a fine stream into about 25 liters of water with thorough agitation, and washed by decantation until free of sulfates. Yield, 100 to 125 g.

On the large scale the chief difficulty experienced was in obtaining proper temperature control due to the large amount of heat given off by the reaction and the high rate at which it is given off when the reaction once

starts. This difficulty was overcome by the use of steam in the cooling coil for the first three minutes in order to give a local high temperature and insure the reaction starting before the concentration of permanganate was so high as to cause excessive temperatures and foaming when the reaction finally started. The precipitate was washed by decantation, which with a 230 kg. lot in a 38-cu. meter tank required 8 to 9 washings.

*Preparation of Copper Oxide.*—Ninety-five g. of copper sulfate pentahydrate is dissolved in 200 cc. of hot water and heated to the boiling point. Thirty-four g. (actual total alkalinity) of sodium hydroxide is used in the form of a lye of about 1.35 sp. gr. The hot copper sulfate solution is added to the alkali with agitation and uncontrolled increase in temperature, the final temperature being usually 60 to 70°. After thorough stirring, the mixture is diluted to a suitable volume for washing and washed by decantation until the sulfates are practically all removed. Yield, about 30 g.

*Preparation of Cobaltic Oxide.*—Fifty-one g. of cobalt sulfate heptahydrate is dissolved in 200 cc. of cold water. This solution is added to 25 g. of sodium hydroxide as lye of about 1.35 sp. gr., and 8.6 g. of sodium hypochlorite (actual, by titration) is then added in the form of a 10% solution with constant agitation. After stirring for about 5 minutes the mixture is diluted and washed until practically free from chlorides. Yield, about 15 g.

*Mixing, and Precipitation of Silver Oxide.*—After thorough washing, the manganese dioxide, copper oxide and cobaltic oxide are mixed and the silver oxide precipitated in the presence of the mixture. Two and a half g. of sodium hydroxide (free from chlorides) is dissolved in a small quantity of water and added to the suspension, and then 7.4 g. of silver nitrate dissolved in about 50 cc. of water, is added with thorough agitation. The silver nitrate is equivalent to about 5 g. of  $\text{Ag}_2\text{O}$ . After the mixed precipitate is washed practically free from dissolved salts, the subsequent treatment is essentially the same as that of the 2-component mixture, which will be described below.

*Preparation of the Two-component Mixture.*—The manganese dioxide for use in the 2-component mixture is prepared in the same way as that used in the 4-component mixture. The copper is precipitated as the basic carbonate rather than the hydrated oxide and the precipitation is preferably carried out in the presence of the precipitated and partially washed manganese dioxide.

*Preparation of Basic Copper Carbonate.*—Ninety-five g. of copper sulfate pentahydrate and 55 g. of anhydrous sodium carbonate are each dissolved in 200 cc. of hot water, the soda solution added to the suspension of manganese dioxide and the copper sulfate solution added to the mixture

with thorough agitation. After a few minutes the mixture is diluted and washed by decantation until practically free from sulfates. The copper sulfate is equivalent to about 30 g. of  $\text{CuO}$ .

**Filtration and Drying of the Precipitates.**—In the case of either mixture the washing is completed, wet-ground fines added if desired and the precipitate filtered in a filter press or on a Büchner funnel. The cake is kneaded, on the large scale mechanically for about 8 minutes, and submitted to a pressure of 4000 to 6000 lbs. per sq. in. between felt pads or camels'-hair cloths to permit the escape of the water. The cakes are dried at about  $50^\circ$ , crushed, screened and the granules redried for 4 hours at  $200^\circ$ , and preserved in sealed containers.

### The Variation of the Activity of the Catalysts with the Method of Precipitation of the Oxides.

Since the oxides prepared by high temperature reactions, as by oxidation of metals or ignition of nitrates, were found to have a much lower activity at ordinary temperatures than those prepared by precipitation, the latter methods of preparation were those most extensively studied. It was found to be desirable in all cases to carry out the precipitations in such a way as to obtain a very finely divided precipitate; thus in precipitating metallic hydroxides concentrated solutions of the reagents were used. Reasonably complete washing is very essential, probably because of the tendency of the soluble salts to collect at the surface of the lumps by capillarity and so decrease the available surface. Of course, in the case of mixtures containing silver oxide, chlorides are particularly undesirable as silver chloride is inert as an oxidation catalyst.

The manganese dioxide is the chief component of both mixtures and hence has a very considerable influence on the activity and hardness. The preparation of it in a finely divided form with a high oxygen content, that is, with a minimum content of lower oxides, is more complicated than that of the other oxides and wider variations in quality were observed. The activity of the various samples was ordinarily tested by making them up into one of the standard mixtures with the other oxides of known activity and testing the resulting mixture with carbon monoxide at room temperature. In some cases, however, they were tested alone in an apparatus in which the temperature of the granules and gas stream could be raised and the temperature determined at which the sample oxidized a carbon monoxide—air mixture with a definite efficiency.

The oxidation of manganese sulfate suspended in sulfuric acid was the method investigated in most detail, since it appeared to lend itself best to large-scale operation, although other methods were tried with more or less success. The simple decomposition of potassium permanganate in conc. sulfuric acid gives a very active product but this procedure is not entirely unattended by risk, for dust particles or other organic matter are oxidized rather violently by the permanganic acid with evolution of

clouds of brown fumes. The product obtained by this reaction is usually darker brown than by the standard method and in the 2-component mixture it dries to a harder granule which is a little more active at low temperatures. The reduction of potassium permanganate in neutral solution by organic compounds such as methyl alcohol gives a fairly active product but at a higher cost than a process obtaining part of the manganese from manganous salts. Processes involving the oxidation of manganous sulfate by potassium permanganate in aqueous solution were uniformly unsatisfactory, the resulting material being soft and practically inactive. This is probably due to the formation of lower oxides and manganites rather than a manganese dioxide free from alkali salts.

In the standard method the reaction is complicated by the decomposition of part of the permanganic acid with evolution of oxygen. The manganese dioxide is not all present as such in the acid mixture but some is present as manganese disulfate,  $\text{Mn}(\text{SO}_4)_2$ , which is hydrolyzed on pouring into water. The material prepared by this method is actually a mixture of oxides and the analysis corresponds with about  $\text{MnO}_{1.85}$ . To a certain extent the available oxygen content is a measure of the activity, but the physical state must also be considered. Since the manganous sulfate is largely suspended in the acid rather than dissolved, it must be finely ground, as otherwise its utilization is very incomplete, only the outside of the particles being oxidized. But the utilization is never entirely complete and the reaction should therefore be carried far enough in the acid mixture to use practically all of the permanganate, to prevent the remainder from reacting on dilution to produce oxides of manganese which are soft and inactive and which seem to have some tendency to coat over and spoil otherwise good material. In the choice of the temperature for the reaction, variations in activity, hardness and yield must be considered. At high temperatures the decomposition of the permanganic acid takes precedence over the oxidation reaction with the consequence that the utilization of the manganese sulfate is very poor, and at temperatures above about  $85^\circ$  the available oxygen content of the product begins to fall off with corresponding decrease in activity. At temperatures below about  $55^\circ$  it is difficult to obtain a complete utilization of the permanganate and the product is generally very soft. The temperatures called for in the directions are those which experimentation has indicated are most suitable for preparing a hard active product. The low temperature at the beginning permits the building up of a high concentration of permanganic acid, and by proper temperature control this is kept in considerable excess throughout the course of the reaction. This is the condition which tends towards the formation of large amounts of manganese disulfate and higher oxides and reduces the formation of lower oxides to a minimum. After the permanganate is all added, the temperature is held at about  $60^\circ$

until the permanganate is practically all used up, which usually requires 10 to 15 minutes. Too long a time is to be avoided as there is a tendency for the manganese sulfate on the inside of the lumps to react with the higher oxides or manganese disulfate giving lower oxides on dilution. A reaction of this type is shown by the mixture becoming thick and granular on standing and the color changing from a dark brown to a dirty purple. The method of dilution is quite important as it has a great effect on the hardness of the resulting material. In order to obtain a high degree of dispersion of the precipitate, the hydrolysis of the manganese disulfate should take place rapidly. This is accomplished by having the acid mixture enter a large amount of water in fine streams and with adequate stirring.

The methods of precipitation of copper oxide were studied largely in connection with the preparation of an absorbent for arsine although in the later work on carbon monoxide the copper oxide samples were tested by making them up into mixtures as in the case of the other oxides. More care is necessary to prepare a copper oxide that will oxidize arsine completely at room temperature than is necessary in preparing copper oxide for use in the 4-component mixture, due probably to the fact that the physical texture of the mixture is largely a composite of that of the components while with a single oxide such equalizing factors are absent. The method used in the preparation was to mix rather concentrated solutions of sodium hydroxide and copper sulfate, boil for various lengths of time, and dilute, wash and filter. In general it was found that the samples of copper oxide most active as oxidizing agents for arsine were those consisting of a rather soft porous granule. The hardness could be controlled by the conditions of acidity or alkalinity at the end of the precipitation. A precipitation with considerable excess alkali gave a precipitate which was slow in settling and hard to filter, and which dried down to a hard dense, black mass with low activity. The sodium hydroxide used contained about 4% of sodium carbonate and with insufficient amounts of alkali, carbon dioxide was evolved as the last of the copper sulfate solution was added. Under these conditions the precipitate was brownish-black with a green tinge. Such samples were active but rather soft for a satisfactory granule. The optimum conditions for an active yet fairly firm granule were found between these two extremes. By carefully controlling the amount of sodium hydroxide or by using an excess and then partially neutralizing with sulfuric acid, these conditions were realized. The correspondence between physical properties and the alkalinity of the solution is that which would be expected from the tendency of the precipitate to coagulate in acid solution and redisperse in alkaline. The low activity of the samples prepared with a large excess of alkali is probably to be attributed to a reduced porosity in the very dense granules. The catalytic oxidation of arsine affords a good example of the action of promoters, for it was

found that soaking the granules in a solution of  $\frac{1}{2}$  % of their weight of silver nitrate and drying materially increased the activity of poor samples. The life of catalysts for the oxidation of arsine at low temperatures is of course limited by the deposition of metallic arsenic or oxides.

Since the hardness of the copper oxide was more readily controlled than that of the manganese dioxide, it was usual, in order to obtain the maximum hardness of the 4-component mixture consistent with high activity, to prepare a harder copper oxide than if it were to be used alone. For this reason an excess of alkali was used and the partial neutralization omitted in the standard procedure for preparing the 4-component mixture.

The precipitation of basic copper carbonate by the addition of copper sulfate solution to sodium carbonate solution results in a material which is very soft when dried and partially converted into the oxide by heating. Judging from the activity of basic copper salts in the oxidation of arsine, it was thought that an increased activity might be obtained on substituting such basic copper carbonates for the ordinary hydrated copper oxide in the 4-component mixture, but this desired effect was not realized in the experiments performed. This was probably due to the formation of silver carbonate in place of part of the silver oxide, since some preliminary experiments indicated that silver carbonate is less active than silver oxide. That the basic copper carbonate is more active than the oxide, at least in mixtures, is indicated by the fact that the 2-component mixture made up with the latter has only a slight activity in comparison with the standard 2-component mixture. This latter mixture tends to give an excessively soft granule, but this can be overcome by pressure.

The experiments of Wright and Luff had shown that cobaltic oxide is remarkably active in the oxidation of carbon monoxide at low temperatures. Hüttner<sup>10</sup> and others had shown that cobalt oxide, prepared under certain conditions, contains more oxygen than corresponds to the formula  $\text{Co}_2\text{O}_3$ , due to the presence in the mixture of a cobalt peroxide or dioxide. It was thought that such cobalt oxide mixtures would probably be more active than those of lower oxygen content, and this was found to be the case, properly prepared samples oxidizing carbon monoxide—air mixtures catalytically at room temperatures. Hüttner used sodium hypochlorite or alkaline solutions of iodine, and in the latter case obtained a higher ratio of oxygen to cobalt. Preliminary experiments did not indicate any advantage in the use of iodine, and most of the samples were made using hypochlorite as the oxidizing agent.

Because of the effect of cobalt oxide on hypochlorite solutions, catalyzing their decomposition with evolution of oxygen, it is necessary to use an excess of 25 to 50 % of hypochlorite to obtain a high ratio of oxygen to cobalt. The effect of temperature of precipitation on the oxygen content

<sup>10</sup> Hüttner, *Z. anorg. Chem.*, **27**, 81 (1901).

of the precipitate is slight provided sufficient hypochlorite is used to offset the more rapid decomposition at the higher temperatures. When a sufficient excess of hypochlorite and of hydroxide was used and the precipitate thoroughly washed no difficulty was experienced in obtaining a comparatively soft, porous, active granule; in fact, the samples were frequently so soft as to be difficult to handle in the tests. The only samples which were hard and lacking in activity were those prepared with insufficient hypochlorite, and the poor activity of these samples was probably due rather to the low oxygen content than to the low adsorptive properties.

While in many cases the activity of a mixture of catalysts is merely a composite of the activities of the several components, it has often been found that mixtures of catalysts are more active than any of their components. The complete explanation of this co-activation of catalysts is still lacking, but the results of the present investigation indicate that the chemical nature of the components and the physical properties of the mixture are very important factors. The use of mixed catalysts was found to be quite essential in obtaining the requisite activity towards carbon monoxide at low temperatures. Of the common oxides tried, none acted alone as an active catalyst with the exception of cobaltic oxide. The latter, however, is itself a mixture of oxides, since, as prepared, the ratio of oxygen to cobalt is about 1.6:1.

A comparison of the activity of the 2-component mixture and its components is given in Table I. The tests were made with a 1% carbon monoxide—air mixture at a space velocity of 6000 cc. of mixture per hour per cc. of catalyst. The oxides were prepared under suitable conditions for obtaining active catalysts and were in the form of 8- to 14-mesh granules in a layer 5 cm. deep as previously described. The temperatures given are those of the entering gas, and the exterior of the catalyst tube was maintained at practically the same temperature. The efficiencies are the percentages of gas oxidized after the conditions became constant.

TABLE I.

Comparison of the activities of the 2-component mixture with Those of Some Single Oxides.

Oxide.	Dry Gas.		Humidity 14mm.	
	Temperature. ° C.	Efficiency. %.	Temperature. ° C.	Efficiency. %.
CuO	102	97	102	18
MnO <sub>2</sub>	100	96	100	17
Co <sub>2</sub> O <sub>3</sub>	0	100	78	100
Fe <sub>2</sub> O <sub>3</sub>	100	40	...	...
MnO <sub>2</sub> + CuO	-10	100	76	100

The last two columns illustrate the characteristic effect of humidity which will be discussed later. The increased activity of the 2-component mixture over the activity of the copper oxide and manganese dioxide



alone is very marked. The co-activation is seen to have lowered, by more than  $100^{\circ}$ , the temperature required in the case of dry gas for 100 % efficiency. As has been stated, the 2- and 4-component mixtures were the most satisfactory from the standpoint both of activity and cost, but, of the large number of mixtures prepared, there were a few others that were fairly active. It was found that manganese dioxide and silver oxide gave an active catalyst, but not materially better than the standard 2-component mixture. A 3-component mixture consisting of 50 % manganese dioxide, 30 % cupric oxide and 20 % cobaltic oxide was found to be active towards dry carbon monoxide—air mixtures but it had much less tolerance towards humidity than the standard 4-component mixture. Some samples of nickelic oxide were prepared in the same way as the cobaltic oxide and substituted for the latter in the 4-component mixture. These mixtures did not operate catalytically towards dry gas for an indefinite length of time at room temperature. The oxidation of the carbon monoxide was accompanied by gradual reduction of the catalyst and loss of activity unless the temperature was slightly elevated. Ferric oxide was found to be even less active than nickelic oxide in these mixtures.

#### The Effect of Kneading and Pressure upon the Activity and Hardness of the Catalysts.

After the oxides are precipitated, washed and mixed, or preferably in many cases precipitated in the presence of each other, subsequent treatment, with the exception of drying, has more effect on the hardness than on the activity. In cases where the catalyst is used under unfavorable conditions, for instance, with some moisture in the gas—air mixture or at low temperatures (as at  $-15^{\circ}$ ), the oxidation of the carbon monoxide takes place to a greater or less extent at the expense of the available oxygen of the catalyst itself, and is terminated by the exhaustion of the catalyst. The life of a given volume of the catalyst under these conditions is dependent, of course, upon the amount of available oxygen present, which in turn is dependent upon the density. A high density also is advantageous in that the heat of the reaction tends to give a higher temperature within the denser granules which favors the re-oxidation of the reduced catalyst and hinders the adsorption of moisture.

The effect of kneading and high-pressure filtration upon the hardness and density of the catalysts was studied in some detail because of its importance in the utilization of fines and in preparing a satisfactory granule from the 2-component mixture. Even after filtering the mixed precipitates at a pressure of 7 kg. per sq. cm. (100 lb. per sq. in.) and blowing the excess water out of the cake by compressed air, the moisture content of the material is still about 60 %, although part of this is water of hydration of the oxides. It was found that kneading broke up the structure of the

cake so that the mass became much more fluid, and additional water could be pressed out at the same pressure if desired. Even without the second pressing, the mass on drying had a greater density and hardness, if the kneading was not excessive. This is doubtless due to a breaking down of the lamellar structure of the cake as it is formed in the filter press, permitting a closer packing of the particles. The data obtained in one series of kneading experiments are presented in Table II. A considerable amount of cake was kneaded in a Werner and Pfleiderer kneading machine and small samples removed at the times indicated. Unfortunately the hardness was not determined in this series but it was found that in general the increase in hardness was somewhat less than the increase in apparent density and the maximum was reached sooner. With the type of kneading machine used, the maximum hardness was usually reached in 6 minutes and the maximum density in 9.

TABLE II.  
Effect of Kneading.

Time of kneading. Min.	Apparent density.	Volume activity.	Weight activity.
0	0.57	32	56
1	0.59	37	63
3	0.64	53	83
5	0.66	55	83
7	0.72	65	90
9	0.75	67	89
11	0.72	64	88
14	0.67	54	81

The column headed "Volume activity" gives the number of minutes that the given volume of sample operated above 85 % efficiency on 1 % carbon monoxide—air containing 14 mm. of water vapor. The "Weight activity" is the volume activity divided by the apparent density, these values of course being only relative. All of these samples were catalytic for an indefinite time on dry gas. The effect of kneading on activity is largely indirect, in that the increased density permits the reaction to go on for a longer time when it is taking place at the expense of the oxygen of the catalyst itself. The occurrence of maxima in the apparent density and hardness curves is probably due to the inclusion of air bubbles in the more thoroughly kneaded samples. The fact that hand kneading gave uniformly better results than machine kneading points towards the same conclusion, for in hand kneading there is less opportunity for the inclusion of air, although the superiority of hand kneading may be due in part to the packing or settling action in comparison with the rubbing action of machine kneading.

The experimentation with regard to hydraulic pressing was concerned chiefly with the utilization of fines, as with the 4-component mixture

it is possible to prepare a reasonably firm granule without the use of hydraulic pressure, except when fines are added. With the 2-component mixture, however, hydraulic pressure is necessary in order to prepare a granule of satisfactory hardness. In order to utilize the fines formed in the crushing operation, they were ground wet in a ball mill to a fine slime and added to the original precipitate and the mixture filtered. If this cake were dried immediately the product would be much too soft for use in gas masks, but by subjecting the cake, after kneading, to high pressure between felt pads to permit the escape of the water, a product is obtained of hardness similar to that of the original material or better. The density is usually somewhat higher and the activity at least as good. The action of high pressure is largely to reduce shrinkage in drying to a minimum and so eliminate shrinkage cracks as far as possible. The results of a typical series of experiments with the 2-component mixture and varying proportions of wet ball-milled fines are presented in Table III. The material was all from a single set of precipitations. The cakes were kneaded for 7 minutes and pressed between felt pads, the pressure being raised gradually and held at the final value for about 5 minutes to permit the escape of the water. At the higher pressures the cake was reduced in thickness from 25 mm. to about 10 mm.

TABLE III.  
Effect of High-pressure Filtration.

Fines. %.	Pressure. lbs./sq. in.	Hardness. %.	Apparent density.	Volume activity.	Weight activity.
50	80	20	0.55	32	58
50	1000	56	0.60	52	87
50	2000	60	0.62	50	81
50	4000	56	0.68	53	78
40	80	27	0.57	48	84
40	1000	76	0.61	52	85
40	2000	65	0.64	53	83
40	4000	78	0.69	53	80
40	6000	90	0.72	63	87
30	80	32	0.56	35	63
30	1000	64	0.62	50	81
30	2000	62	0.65	54	83
30	4000	62	0.69	55	80
30	6000	62	0.73	66	80

These figures show that the apparent density and volume activity increase quite regularly with the pressure applied to the cake. The hardness figures do not show so much regularity, but this is largely due to inherent errors in the hardness determination, which are particularly evident in this series because the method had not yet been thoroughly standardized. A hardness of 70 on this scale may be interpreted as quite

sufficient for gas-mask use. It is evident that the apparent density is not a satisfactory criterion of hardness when the mixtures contain fines. The content of fines may be increased above 50 %, in fact the use of wet ball-milled fines alone gave fairly satisfactory results, when thoroughly kneaded and pressed at high pressure.

The discussion of the effect of the degree of drying on the activity of the catalysts will be postponed until after the effect of the humidity of the gas mixture has been considered.

### **The Effect of the Conditions of Operation on the Activity of the Catalysts.**

Under the conditions of operation used in the standard tube-tests with dry carbon monoxide—air mixtures at room temperature, that is, using a 5 cm. layer of 8- to 14-mesh granules and a rate of flow of 500 cc. of 1% gas per sq. cm. per minute, good samples of either the 2- or the 4-component mixture operate at efficiencies closely approaching 100 % for an indefinite length of time. Such samples also operate at high efficiency on more dilute mixtures as shown by tests with concentrations of 0.1% or less. The theoretical temperature rise under adiabatic conditions due to the heat of the reaction is about 100° for a 1% mixture. Because of this heat effect, little difficulty is experienced in obtaining a complete oxidation at higher concentrations even with rather poor samples, although with concentrations much above 5 % the temperature rise may be sufficient to impair the activity of the catalyst after cooling. With very high concentrations the catalyst may even sinter together and be entirely inactive when cold.

The activity of the catalysts at low temperatures is of course very important when they are to be used in gas masks in exposed locations. The effect of the temperature of the carbon monoxide—air mixture on the activity is masked somewhat by the heat of the reaction, but it can be determined readily by using dilute gas mixtures so that the heat effect is small. In general for each particular sample of catalyst and gas concentration there is a minimum temperature at which the catalyst operates catalytically at 100 % efficiency. Below this temperature the efficiency gradually falls off to a more or less constant value for each temperature but returns again to 100 % when the temperature is raised. Most of the tests were made with 0.5 % carbon monoxide and the catalyst was placed in a glass tube surrounded by a freezing mixture so that there was little opportunity for it to heat up by the heat of the reaction. It was found that the 2-component mixture operated better at low temperatures than the 4-component mixture although individual samples varied somewhat, especially when there were variations in the methods of pressing and drying. The samples prepared with high pressure were much better than those

filtered at comparatively low pressures and adequate drying was found to be quite essential. A typical sample of the 2-component mixture, when tested with 1% carbon monoxide at  $-15^{\circ}$ , operated initially at high efficiency, but after a few minutes the efficiency began to fall and gradually decreased to about 35 % where it remained in apparent equilibrium. When the temperature of the gas and catalyst tube was allowed to rise to  $0^{\circ}$ , the efficiency gradually rose to 100 %. Similar experiments on manganese dioxide and copper oxide alone at higher temperatures indicated that under proper conditions this phenomenon is accompanied by reversible reduction of the catalyst, that is, the catalyst is partially reduced at the lower temperature and reoxidized at the higher. This reduction is different from that obtained by treating the catalyst at a high temperature with carbon monoxide or other reducing agents in the absence of an excess of oxygen for in this case the reduction is more complete and is usually accompanied by a change in structure. The activity cannot then be restored by re-oxidation with air.

The general effect of water vapor in the gas mixture is to diminish the activity of the catalysts so that higher temperatures are necessary for definite efficiencies than when operating with dry gas. Somewhat the same effect is brought about by a diminution of the oxygen content of the gas. While, in gas-mask use, the oxygen requirements of the man are so high that such effects do not enter under any conditions under which a man could live, they are of importance in connection with the application of the catalysts to the removal of carbon monoxide from hydrogen by preferential combustion and in other industrial applications. It was found that for an equilibrium efficiency of 100 % with 28 mm. of water vapor, reducing the oxygen content of the gas to as low as 100 % excess of that theoretically required for the combustion only necessitated an increase of temperature of about  $10^{\circ}$  over the temperature required with a carbon monoxide—air mixture containing the full oxygen content. It was also found that when operating with the 2-component mixture on a mixture containing 0.5 % carbon monoxide, 0.5 % oxygen and 55 mm. of water vapor at a space velocity of 6000 cc. of gas per cc. of catalyst per hour, 190 hours of continuous operation at  $102^{\circ}$  and an average efficiency of 93 % did not result in any appreciable deterioration of the catalyst.

The humidity of the carbon monoxide—air mixture has a very marked effect on the activities of the various oxides and mixtures. The effect is best described as reversible poisoning, to distinguish it from the type of poisoning brought about by sulfur compounds and some of the war gases. While the 2-component and 4-component mixtures act catalytically for an indefinite length of time on dry gas mixtures at ordinary temperatures, with 1% gas mixtures half saturated with water vapor at room tempera-

ture the activity falls to 85% in about an hour and rapidly decreases from then on. If the mixture is changed from wet to dry at any time before the catalyst has stopped acting, the efficiency gradually returns to the original value of about 100% in the case of active samples. The rate at which the efficiency of the catalyst decreases is a function of the temperature at which the test is made and hence indirectly of the concentration of the gas, since the heat of the reaction raises the temperature of the catalyst. At temperatures somewhat above room temperature, the catalytic oxidation proceeds indefinitely even with gas mixtures of high humidity.

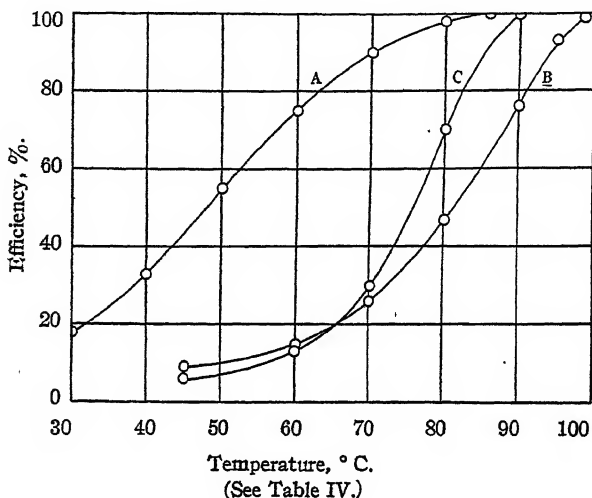


Fig. 1.

At intermediate temperatures and humidities, the activity does not fall to zero but only to a fairly definite value for any particular sample of catalyst. These efficiencies are approximately the same when approached from either side if sufficient time is allowed for conditions to become constant. The variation of these equilibrium efficiencies with the temperature is shown by the data of Table IV, which have been plotted in Fig. 1. In obtaining these results the catalyst was placed in a copper tube immersed in a water-bath which was maintained at the desired temperature, and the gas was preheated by passing through another tube immersed in the bath. The bath was held at each temperature long enough for constant efficiency to be obtained. While these results are of interest from the standpoint of the mechanism of the reaction, the equilibrium efficiencies at ordinary temperatures are so low for the usual humidity that the time necessary for the efficiency of the dried catalyst to fall to a definite value is of greater importance in connection with the application

TABLE IV.

Variation of Equilibrium Efficiencies with the Temperature.

Catalyst: Humidity.	Curve A. 4-component. 28 mm.	Curve B. 2-component. 55 mm.	Curve C. 2-component. 55 mm.
Composition	CO 0.25	CO 0.5	CO 1.0
of gas, %.	Air 99.75	O <sub>2</sub> 0.5	O <sub>2</sub> 1.0
		N <sub>2</sub> 99.0	N <sub>2</sub> 98.0
	Temp. °C.	Temp. °C.	Temp. °C.
	Effic. %.	Effic. %.	Effic. %.
	40	45	45
	33	9	6
	50	60	60
	55	15	13
	60	70	70
	75	26	30
	70	80	80
	90	47	70
	80	90	90
	98	76	100
	87	95	..
	100	93	...
	..	98	99
	...	99	..
			...

of the catalysts to gas masks. It was found that this time was materially shorter at low concentrations where the heat effect of the reaction was small. This is shown in another way by the data of Table V, which represents the results of a series of experiments in which air at room temperature containing 4 mm. of water vapor was passed through a 5 cm. layer of the 2-component mixture at the rate of 500 cc. per sq. cm. per minute for a definite length of time and followed by 1% carbon monoxide also containing 4 mm. of water vapor.

TABLE V.

Time of humidification. (Min. of air flow.)	Life to 85% efficiency. (Min. of gas flow.)
0	236
30	128
45	74
60	4

Other experiments have shown that, when air of 4 mm. humidity is passed over the catalyst dried in the usual way, the moisture in the air is absorbed practically completely during the first hour. These results indicate that an absorption of water equivalent to about 3.6% of the weight of the catalyst is sufficient to reduce the efficiency to 85%. It is evident, therefore, that the dryer used in the canister must be quite effective in order to protect the catalyst from moisture.

The tests referred to hitherto were all made with the standard rate of flow of 500 cc. per sq. cm. of cross section per minute and with a depth of layer of 5 cm., that is, with a space velocity of 6000 cc. of gas per cc. of catalyst per hour. In the design of gas-mask canisters it is desirable to

reduce the resistance to the minimum consistent with efficient operation of the catalyst. The resistance is of course dependent upon the size of the granules and the area and depth of layer. As the size of granules is increased and the depth of layer decreased, there evidently must come a time when the oxidation is incomplete because the molecules of carbon monoxide do not all have an opportunity to come into contact with the catalyst. Since this effect is not due to insufficient activity of the catalyst itself, it is referred to as mechanical leakage. In order to determine approximately the conditions under which mechanical leakage begins to be appreciable, a series of experiments was performed with a constant space velocity of 7800 but with varying size of granules and depth of layer. The results of these experiments are presented in Table VI. The equilibrium efficiencies were rapidly attained and remained constant except for slight fluctuations. No mechanical leakage was encountered at this space velocity with layers 2 cm. or more thick and 10 to 14 mesh or finer.

TABLE VI.

Efficiencies with Various Sizes of Granules and Depths of Layer.

	Depth, cm. Rate of flow, cc. / sq. cm. / min.	2. 260.	1.5. 195.	1. 130.
Mesh, 10-14 .....		100%	99.0%	96.5%
Mesh, 14-20 .....		100	99.8	<del>98.7</del>
Mesh, 20-28 .....		100	100	99.5
Mesh, 28-35 .....		100	100	99.8

The pressure drop at these rates of flow varied from 12 mm. of water for a 5cm. layer to about 0.2 mm. for a 1cm. layer of 10- to 14-mesh material. It is evident from these figures that the use of the catalyst in the form of granules gives a very satisfactory contact with the gas without at the same time introducing an excessive resistance to the flow.

The high degree of porosity of the catalysts and their consequent high absorptive power for many volatile substances has been mentioned. Many of these substances, particularly sulfur and halogen compounds, act as poisons and tend to prevent the catalytic oxidation of carbon monoxide. It might be thought that the sensitiveness of the catalysts to poisons would seriously interfere with their practical use in gas masks, but such is not the case for the catalyst may be protected readily from large concentrations of poisons by a layer of activated charcoal in the canister, while with small concentrations the poisoning is progressive, the first layers of the catalyst absorbing practically all of the poison leaving the rest of the catalyst available for the oxidation reaction.

#### The Effect of the Degree of Drying on the Activity of the Catalysts.

The usual method of drying was that indicated by preliminary experiments to give satisfactory results, namely drying the filter cake at about 120°, crushing to size and redrying at 200° for about 4 hours. Additional



experiments were made to test the effects of drying *in vacuo* or at higher temperatures. A fairly large sample of 2-component cake after hydraulic pressing was ground and bottled after thorough mixing to insure a uniform distribution of grains of slightly different moisture content. The loss of weight on drying was determined and the dried samples were tested with 1% carbon monoxide—air mixture containing 14 mm. of water vapor. The results are given in Table VII.

TABLE VII.  
Effect of Degree of Drying.  
Conditions of Drying.

Expt.	Temp. °C.	Time. Hrs.	Pressure. Mm.	Loss in weight, %.	Life to 85% efficiency, Min.
16	100	3	12	37.0	41
17	400	5	12	47.3	51
20	{ 120	15	Atm. }	39.9	52
	{ 200	5	Atm. }		

The catalyst dried as in Expt. 17 did not lose more than 0.1% of water when heated to redness in a current of air in a quartz tube, and this small amount was probably absorbed from the air while the material was being placed in the tube. Analysis indicated that drying at 400° entailed a loss of available oxygen of 0.6% on the original wet weight. Allowing for this, the moisture content of the material after drying as in Expt. 20 is about 11.5%. Other experiments have shown that the moisture content may be as high as 14% without seriously decreasing the life of the catalyst on moist gas, and this is not increased much by more complete drying. These results are interesting in connection with the data of Table V, which showed that the moisture absorbed during the test with gas containing 4 mm. of water vapor was only about 3.6%, which is only a fraction of the water removed on complete drying, yet the completely dried samples have approximately the same life with moist gas as the incompletely dried ones. This indicates that the moisture absorbed from the gas remains for the most part as a film on the surface of the catalyst, hindering the adsorption of the gas molecules and oxygen molecules, and does not re-hydrate the oxides to any considerable extent.

The properties of the 4-component mixture proved to be somewhat different, in that a sample after the usual drying at 200° contained only 4.5% of residual water. Tests with 1% gas containing 14 mm. of water vapor gave a life of 58 minutes to 85% efficiency for the sample after standard drying, but a life of only 25 minutes after complete dehydration at 400° and 12 mm. This is probably due to partial decomposition of the silver oxide under these conditions.

### Application of the Catalysts.

While in the foregoing the activity of the catalysts has been discussed principally in connection with the oxidation of carbon monoxide, it has

been found that these catalysts are able to reduce materially the temperature required for the oxidation of a variety of gaseous reducing agents by atmospheric oxygen. For continued catalytic action it is necessary, however, that neither the reagents nor the products should poison the catalysts and that the temperature of operation should not be so high as to cause injury to the catalysts by sintering or loss of oxygen. Because of the possible industrial applications, some attempts were made to apply the catalysts to organic oxidations in the vapor phase, such as toluene to benzaldehyde and naphthalene to phthalic anhydride. It was found that with the 2-component mixture, the oxidations started at the comparatively low temperatures of 170° and 220° respectively, but that it was very difficult to prevent the reaction from going too far with the formation of carbon dioxide and water as the principal products. This was due largely to the difficulties inherent in controlling the temperature of operation. The heat evolved in such organic oxidations, particularly when the reaction goes to completion, is very considerable in amount and the proper dissipation of it is a serious problem. The factors such as high porosity and fineness of particles which give the catalysts their high activity are also the ones which render them poor conductors of heat and this makes temperature control by cooling the walls of the catalyst chamber very unsatisfactory. Since other methods of temperature control are inconvenient, it seems probable that the catalysts would have to be considerably modified in order to make them suitable for organic oxidations.

### Summary.

A description is given of some active catalysts developed by the Chemical Warfare Service for use in gas-mask canisters as a protection against carbon monoxide. These catalysts are mixtures of metallic oxides, the two most satisfactory mixtures containing manganese dioxide and basic copper carbonate, and manganese dioxide, copper oxide, cobaltic oxide and silver oxide respectively. These mixtures oxidize carbon monoxide rapidly and completely at ordinary temperatures, and, when protected by a drying agent such as calcium chloride, are suitable for use in gas masks against the concentrations of carbon monoxide ordinarily met with except under conditions where an oxygen helmet is necessary because of the reduced oxygen content of the air. The factors influencing activity, such as the constituents of the mixtures, the conditions of precipitation, the mechanical treatment of the precipitate and the method of drying, are discussed and a description is given of the performance of the mixtures under various conditions of operation.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

**THE DETERMINATION OF THORIUM IN MONAZITE SAND  
BY AN EMANATION METHOD.**

BY HOMER H. HELMICK.

Received March 21, 1921.

**Historical.**

In a recent paper,<sup>1</sup> Cartledge described an "emanation method" for the determination of thorium in monazite sand which was based on the facts: (1) thorium is the first member of the series of radioactive elements now known as the Thorium Series; (2) one of the members of the series, thorium emanation, is a gas. As a further basis for his method, he assumed: (1) on account of the great age of monazite, the elements of the thorium series have reached "radioactive equilibrium," (2) in an acid solution of monazite sand, the emanation is in such a condition of availability that it can be practically completely swept out by bubbling air through the cold solution. In our work on this problem, we have accepted the same facts and made the same assumptions.

Cartledge states that his method "by a triplicate analysis will give the thorium content within 1.5 % of its true value," and pointed out that the inability of the method to give results of a higher degree of accuracy was probably due to the adsorption of thorium X by the undissolved material in the final solution, by the filter paper employed in the process of making the solution, and on the walls of the vessels used. Assuming that he was correct as to the sources of error, it was obvious that a much greater degree of accuracy could be obtained if a method could be perfected which would produce a complete solution of the sand without filtration and which would require the use of but one vessel. A thorough study of this problem led to a very satisfactory solution.

**Proposed Method and Apparatus.**

The method developed in this paper involves the following experimental steps: (1) preparation of the sample, (2) fusion, (3) solution of the melt, (4) transfer to solution vessel, (5) measurement of the ionization due to the sample. The preliminary investigation of each step will be recounted in order.

(a) **Preparation of the Sample.**—No difficulty was experienced in connection with this step, the same method being used throughout the experiments and in the final method. The sample was simply weighed out from a quantity of well-mixed, finely divided and dried monazite sand. Details are given under the description of the final method in the latter part of this paper.

<sup>1</sup> Cartledge, *THIS JOURNAL*, 41, 40 (1919).

(b) **Fusion.**—It occurred to us that a fusion of monazite sand with a suitable flux might prove a satisfactory substitute for the acidified water solution used by Cartledge, inasmuch as a fusion would eliminate loss of thorium X through filtrations and use of several vessels. Fusions were therefore made of monazite sand with (1) potassium hydrogen sulfate, (2) equal parts sodium carbonate and potassium carbonate, (3) anhydrous metaphosphoric acid. We were unable to sweep any emanation out of the potassium hydrogen sulfate melt, so it was eliminated from further consideration. The alkali carbonate melt was also abandoned because of the considerable percentage of sand remaining undecomposed, the violent effervescence, and the high temperature necessary. The fusion with anhydrous metaphosphoric acid appeared most promising, proceeding fairly quietly at about  $700^{\circ}$ , giving a melt only moderately viscous and leaving very little material undecomposed. Many experiments in our later work showed that this small amount of undecomposed material, chiefly silica and ilmenite, was the probable cause of disturbing effects on account of adsorption of thorium X. This difficulty was overcome by the addition of potassium hydrogen fluoride and metaphosphoric acid during the fusion in such a way that hydrogen fluoride was produced in the fused mass at a high temperature as well as practically continuously for some time, these conditions being found necessary for the removal of the objectionable compounds of silicon and titanium in the form of volatile fluorides. The detailed procedure is given in the latter part of this paper.

(c) **Solution of the Product of the Fusion.**—Our original plan had been to sweep the emanation directly out of the fused mass by bubbling air through it; but we were unable to find a vessel which would be inexpensive and at the same time both withstand the action of the hot fused material and resist deformation by pressure necessary to force air through the fused mass. It seemed that a platinum vessel would be necessary; but at this point a consideration of the chemical nature of monazite sand and the appearance of the cold metaphosphoric acid melt prompted us to attempt to dissolve it in water. This was found possible but extremely slow. To speed up solution a solvent was needed which had a high boiling point. Ordinary orthophosphoric acid immediately suggested itself, and experiment showed that our fusion of monazite sand could be fairly rapidly dissolved in 80 % orthophosphoric acid at  $240\text{--}250^{\circ}$  in a platinum crucible, the product consisting of a slightly viscous liquid, easily poured, and the crucible being readily washed out clean with water. Subsequent addition of a small amount of water with stirring produced a practically complete solution. Thus, by fusing monazite sand with metaphosphoric acid and potassium hydrogen fluoride in a platinum crucible, then heating and stirring the resultant mass with 80 % orthophosphoric acid, and finally

adding water, we achieved our original goal of a complete solution (without filtration) in a single vessel. It remained to be seen whether the emanation measurements would justify our expectations of increased accuracy.

(d) **Transfer to the Solution Vessel.**—It would have been ideal if the solution of monazite sand made in a single vessel, as outlined above, could have been left in that vessel during the emanation measurements. We found, however, that this was impracticable on account of the cost of a platinum vessel of the necessary size. We decided, therefore, to transfer the solution as finally produced in a platinum crucible of moderate size to a glass vessel specially designed for the emanation withdrawal. Results have shown that this can be done at a negligible sacrifice of accuracy. Throughout this paper this special glass vessel is called the "solution vessel," and is shown diagrammatically in Fig. 1. It is important that this vessel be made of good glass and have a thin bottom to enable the hot solution (which becomes viscous on cooling) to be poured in without danger; that it be tall and narrow to give maximum deëmanation by the stream of air bubbles; that it have ground-glass connections to prevent leakage and to insure constant length and volume of air line, as well as constant depth of air inlets below the surface of the solution; that it have a trap to prevent mechanical carriage of solution droplets into the ionization chamber; and that the bottom of the stopper be so high above the surface of the solution that only a negligible portion of the solution can be thrown against it by the bursting bubbles. Our experience also showed the most efficient air inlet jets to be those directed upward. The details of the technique used in transferring the hot solution from the platinum crucible to this glass vessel are given in the complete description of the method in the latter part of this paper.

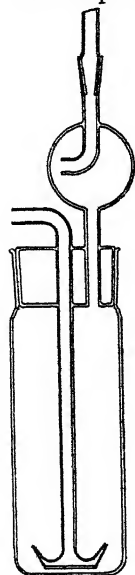


Fig. 1.—Solution vessel ( $\frac{1}{2}$  actual dimensions).

(e) **Measuring Apparatus.**—We have used, with the changes and additions described below, the electroscope and accessories set up by Cartledge. A full description is given in his paper mentioned above, and we will therefore describe only the new parts.

**Insulation Protector.**—In the measuring apparatus as set up by Cartledge it was necessary to dry the stream of air after it had bubbled through the monazite solution before it entered the ionization chamber, in order to prevent the formation of a conducting film of moisture on the amber insulator separating the charged system from the grounded parts of the electroscope and ionization chamber. Cartledge dried the air stream

by means of a tube filled with granular calcium chloride. We examined the effects on the measurements of, respectively (1) this ordinary calcium chloride tube, (2) a much longer tube held horizontally with only the lower

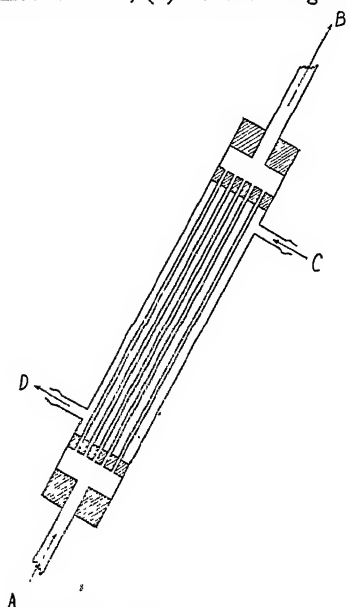


Fig. 2.—Multiple condenser.

A—Air inlet; B—Air outlet; C—Water inlet; D—Water outlet.

half filled with granular calcium chloride, (3) a multiple condenser consisting of many short, small-bore condensers combined in parallel and cooled with running tap water (see Fig. 2), (4) an ordinary short condenser filled with glass beads. None of these driers was entirely satisfactory because of either formation of moist surfaces which apparently adsorbed some emanation, or changes in area of cross-section of air line on account of deposition of water in interstices between granules of drying agent or in interstices between beads, or in small tubes. Since it thus appeared extremely doubtful whether the air stream could be dried without undesirable effects, we abandoned all attempts to do so and directed our attention to direct protection of the insulation. An arrangement was accordingly devised whereby the insulator was directly protected by calcium chloride. The modification of the apparatus is shown in Fig. 3. The air gap between the rod R and the amber  $A_2$  constitutes a better resistance than amber itself. Circulation or diffusion of air through this gap must be slight, and whatever air does reach the amber insulator  $A_1$  is thoroughly dried by the calcium chloride in the wire-gauze basket B. Determinations made with this modification of the apparatus were much more satisfactory in every way than those made when the air was dried before entering the ionization chamber. There were, however, the following objectionable features: (1) the calcium chloride basket had to be taken out and refilled frequently, (2) the capacity of the electroscope seemed to change very slowly and very slightly during a determination, probably on account of the gradual wetting of part of the calcium chloride (mainly near the air gap), (3) uncontrollable and irregular effects due to minute quantities of emanation getting into the insulator chamber (in this article, by insulator chamber we mean the chamber fixed between the electroscope proper and the ionization chamber in this modification of the apparatus). In the apparatus which we have finally adopted, these

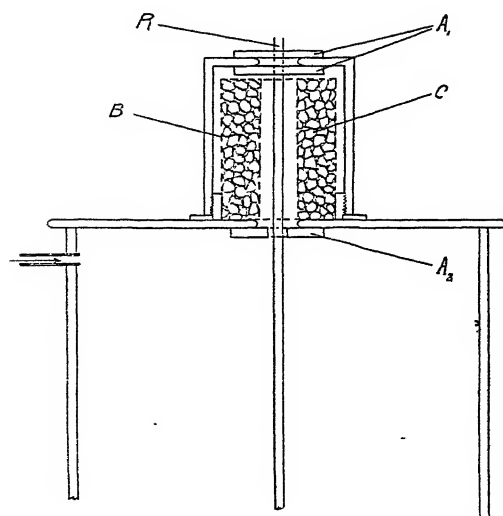


Fig. 3.—Insulator protection (first form).

*R*—Rod to electroscope; *A*<sub>1</sub>—Amber insulator;  
*B*—Wire basket; *C*—Calcium chloride; *A*<sub>2</sub>—  
 Amber plug.

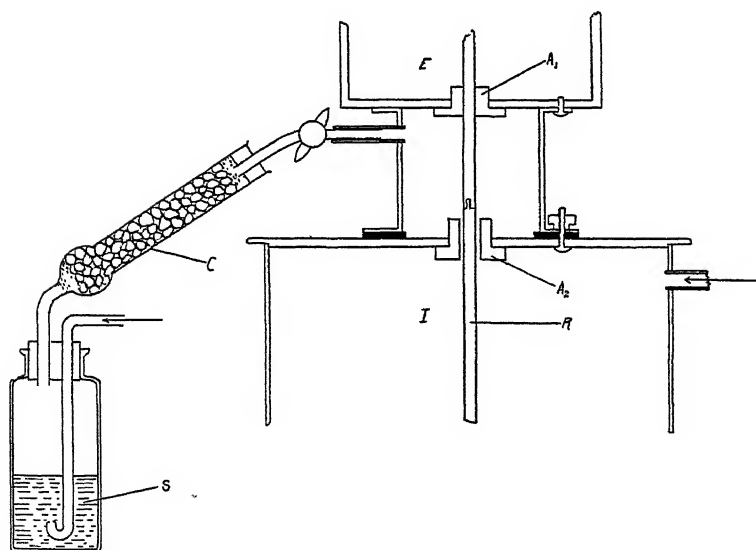


Fig. 4.—The insulator protection.

*E*—Electroscope; *I*—Ionization chamber; *A*—Amber insulator; *A*<sub>2</sub>—  
 Amber plug; *R*—Rod (brass); *S*—CaCl<sub>2</sub> solution (sat.); *C*—Calcium  
 chloride tube.

objectionable features are entirely eliminated by the use of the insulator protector shown in Fig. 4. Outside air is drawn, by the suction from the main "line," very slowly through calcium chloride solution S, thence through calcium chloride tube C, then through the insulator chamber, and finally out through the air gap. The insulator is thus kept constantly in an atmosphere of dry air. This protector functions perfectly, is extremely simple, and requires practically no attention.

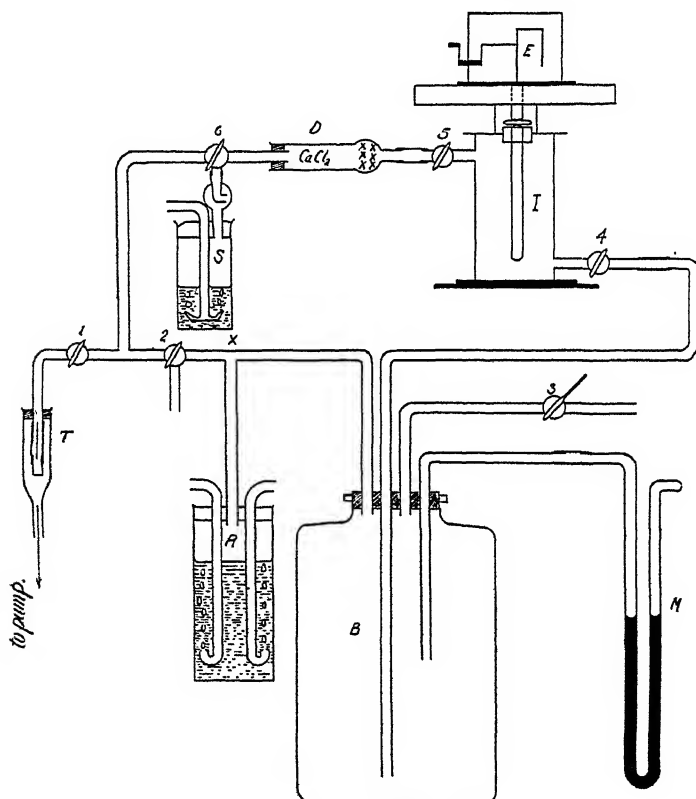


Fig. 5.—Diagram of set-up for emanation measurements.

E—Electroscope; I—Ionization chamber; D—Drying tube; S—Solution vessel; M—Manometer; R—Pressure regulator.

*Pressure Regulator and Optimum Pressure Gradient.*—Our method depends on comparing the rate of discharge of an electroscopes by the emanation from a solution of the "unknown" sample with the rate produced by the emanation from a standard solution. In order that these rates may be directly comparable, it is necessary that the speed with which the emanation is drawn from solution to ionization chamber be the same,



within narrow limits, in both cases. Therefore a constant pressure gradient must be maintained along the suction line. This we have done

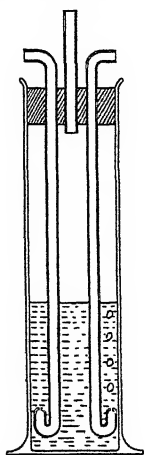


Fig. 6.—Pressure regulator.

by introducing a short branch from a point in the main line (farther from the solution than the ionization chamber) to a pressure regulator. Its relation to the rest of the setup is shown in Fig. 5. For a detailed drawing of the piece, see Fig. 6. Although the drawings show but 2 air inlets, the regulator actually used had 7, all admitting air under almost the same pressure conditions. The liquid used in the regulator is water, and adjustment to desired functioning pressure is attained by adding or subtracting water.

It is desirable, of course, to operate at that pressure at which the pressure coefficient of the rate of discharge of the electroscope is a minimum. A solution of monazite was therefore placed in the apparatus and the rate of discharge of the electroscope determined through the range of practical working pressures (our manometer readings). The results were plotted, the electroscopic readings being taken as ordinates and the pressure (manometer) readings as abscissas. The curve, Fig. 7, shows that the pressure coefficient of the rate of discharge of the electroscope is (for our apparatus) zero when the manometer reading is 11.5 cm. (of olive oil). (For the relation of the manometer to the remainder of the apparatus see Fig. 5.) By working at this pressure we therefore practically eliminated all error due to small pressure variations, attaining at the same time, as the curve shows, the extremely desirable effect of the maximum rate of discharge attainable. Thus, greater accuracy and maximum speed were attained.

#### Detailed Procedure.

**The Sample.**—About 50 g. of the well-mixed monazite sand is weighed out and ground to pass

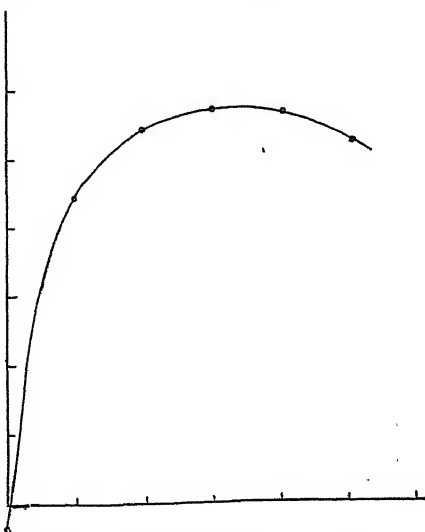


Fig. 7.—Pressure-discharge curve.

through a sieve with 40 wires per cm. It is then thoroughly mixed, placed in a weighing bottle, and dried to constant weight at 115–120°. For a determination a 2.0g. sample is weighed out to within 0.001 g.

**The Fusion.**—The sample is well mixed, by pouring back and forth between sheets of glazed paper, with 5 g. of potassium hydrogen fluoride and 5 g. of anhydrous (recently fused) metaphosphoric acid. The mixture is placed in a 35cc. platinum crucible and brought slowly to the highest temperature of the Meker burner, and heated until no further reaction is apparent. With continued heating, 5 g. more of the metaphosphoric acid is added in small portions, the reaction being allowed to come to completion each time before another portion is added. After the last of the metaphosphoric acid has been added, the mass is allowed to cool, the crucible being rotated in such a way that, when cool, the material is distributed as evenly as possible over the surface of the lower half of the inside of the crucible. The cooled mass is practically transparent and is colorless, and glasslike.

**Solution of the Melt.**—After allowing the fused mass to cool, 20 cc. of 80 % orthophosphoric acid is added to the crucible, which is then placed in an air-bath where it is heated to 250–255° and maintained at that temperature for 3 hours. During that time it is stirred by a platinum wire stirrer attached to a motor. The liquid resulting from this treatment is, at 200–250°, about as viscous as light oil.

**Transfer to Solution Vessel.**—The solution vessel is suspended, to about  $\frac{1}{3}$  its depth, in a bath of conc. sulfuric acid at 190–200°. The stirrer is lifted just above the liquid in the crucible and rotated for a few seconds to free it of most of the liquid adhering to it. Then the liquid is quickly poured out of the crucible into the solution vessel. The latter is now taken out of the hot bath, placed on an asbestos board, and allowed to cool. Twenty cc. of water is run into the crucible, the liquid stirred vigorously for a minute or two and the washings poured into the cooled solution vessel. This operation is repeated with a second 20 cc. of water. Any heavy particles of undecomposed sand and occasionally a little ilmenite still remaining in the crucible are then washed into the solution vessel by using 5 cc. of water blown from a small wash-bottle holding just that amount. The mixture in the solution vessel is now rapidly stirred for at least 15 minutes. The same stirrer is used throughout the experiment. Finally the stirrer is lifted just above the liquid, rotated for a few seconds, and washed with 5 cc. of water from the small wash-bottle, the wash-water being caught in the solution vessel. Water is then carefully added to bring the volume of the solution up to 75 cc. as indicated by a line etched on the vessel. The stopper carrying the inlet tube is then fitted into the solution vessel. A little desiccator-grease is used to insure an air-tight joint.

**The Measurement.**—(For diagram of the apparatus see Fig. 5. The calcium chloride tube D is omitted in our final apparatus.) Measurements are made on 3 different solutions, the blank, the standard, and the "unknown."

*The blank* is run first. This solution may be used for an indefinite number of determinations. It is prepared according to the method for an "unknown" sample as above, except that the monazite sand is omitted. The solution bottle containing the blank is attached to the line in place of Bottle S shown in the diagram. The pump is started, Cocks 1, 3, 4 and 5 are opened wide, Cock 6 is opened wide between S and I, and then Cock 2 is opened between Cock 1 and X. The cock admitting dry air to the insulation chamber (shown in Fig. 4 only) is then opened until the inlet tube through the calcium chloride solution is allowing bubbles to pass in slowly, at the rate of about 10 per minute. Cock 3 is then gradually closed until half the inlets of the pressure regulator are admitting air. We have the regulator so adjusted that the manometer, M, which contains olive-oil, then shows a difference between the pressure in Bottle B and the atmospheric pressure of 11.5 cm. This is best for the reasons given above. Under these conditions air bubbles through the monazite solution at a rate sufficient to stir it rapidly and thoroughly. The time of discharge of the electroscope is then noted.

*The Standard.*—Cock 2 is turned so as to admit air through the side-tube and close the line to the pump. The standard solution is substituted for the blank. Cock 6 is opened between the solution and the pump and a moderate stream of air drawn through the solution for 6 minutes to rid it of radium emanation. The cocks are then adjusted exactly as they were for the blank and readings of the time of discharge taken until constant within the allowable limits for the degree of accuracy desired.

*The Unknown.*—Exactly the same procedure is followed as for the standard.

The ionization chamber is then evacuated for  $\frac{1}{2}$  hour and the pump stopped.

**Calculation of Results.**—The percentage of thorium in the "unknown" may be calculated from the equation,

$$X = A \frac{T_s(T_b - T_u)}{T_u(T_b - T_s)},$$

where  $X$  is the percentage of thorium in the unknown,  $A$  the percentage of thorium in the standard,  $T_s$  the time of discharge of the electroscope by the standard,  $T_u$  the time of discharge of the electroscope by the unknown, and  $T_b$  the time of discharge of the electroscope by the blank. The percentage of thorium in the standard is determined by gravimetric analysis.

## Results.

In the table below are given the results of a series of determinations, showing the separate results of the triplicate analyses of each lot by our emanation method, and the average result from the triplicate analyses of each lot by the gravimetric method of Carney and Campbell. The agreement of the results obtained by our emanation method with those obtained by the gravimetric method is very close.

TABLE OF RESULTS.

Lot no.	Source of monazite.	ThO <sub>2</sub> emanation method. %.	Av. ThO <sub>2</sub> emanation method. %.	Av. ThO <sub>2</sub> gravimetric method. %.
20	India	8.71	....	....
		8.75	8.74	8.76
		8.76	....	....
		8.69	....	....
22	India	8.70	8.70	8.70
		8.72	....	....
		8.49	....	....
23	India	8.53	8.51	8.50
		8.53	....	....
		8.66	....	....
26	India	8.67	8.69	8.69
		8.73	....	....
		8.73	....	....
28	India	8.77	8.77	8.76
		8.80	....	....
		8.67	....	....
30	India	8.68	8.70	8.70
		8.74	....	....
		6.37	....	....
A	Brazil	6.38	6.38	6.38
		6.40	....	....
		4.37	....	....
B	Carolina	4.37	4.39	4.40
		4.43	....	....

## Suggested Further Improvement.

The transfer of the viscous solution of the fused mass in 80 % ortho-phosphoric acid from the platinum crucible to the glass "solution vessel" should be eliminated for the following reasons: (1) it is difficult to carry out successfully, even after much practice; (2) it consumes time, requiring about ½ hour; (3) probable loss of some thorium X on the surface of the platinum and practically inseparable from it even by washing a great number of times. These objectionable features can easily be avoided by the use of a platinum vessel of such size and shape as will allow the final electroscopic determination to be made with the solution in it instead of in the special glass vessel we have used. We suggest, therefore,

that if a great many analyses are to be made, a special platinum vessel be used. Fig. 8 shows the dimensions which we believe such a vessel should have, and a method of connecting the vessel to the line of apparatus.

### Comparison of Methods.

In order that a method of quantitative determination may be useful, it must give results sufficiently accurate for the purpose at hand. Our method does this. In addition to accuracy, the next most desirable feature in a method is speed. In this respect our method is far superior to any other; a complete analysis by any gravimetric method requires approximately 20 hours, whereas our method requires somewhat less than 8 hours. The technique involved is extremely simple except when the transfer from platinum crucible to glass vessel is made, and, as has been suggested above, that would probably not be done if a great many determinations were to be made.

The disadvantages inherent in the emanation method as compared with gravimetric methods are (1) the apparatus required is somewhat costly; (2) the electroscope must be attached to a support practically free from vibration; (3) the electroscopic determinations must be made in a room free from unusual radio disturbances. If a great many analyses were to be made, these disadvantages could be disregarded, since the saving in time attained by the use of this emanation method would soon more than compensate for the initial cost and for the inconvenience in installing and protecting the apparatus.

### Summary.

The main sources of error in Cartledge's emanation method of determining thorium in monazite sand apparently were adsorption of thorium X by suspended matter in final solutions, by filters, and by walls of vessels used. We have avoided these by producing a complete solution of the sand without filtration and in a single vessel. This involves (a) fusion of the sand with metaphosphoric acid and potassium hydrogen fluoride; (b) solution of the resultant mass in hot 80 % orthophosphoric acid. Other improvements made are (1) use of a highly efficient form of vessel to contain

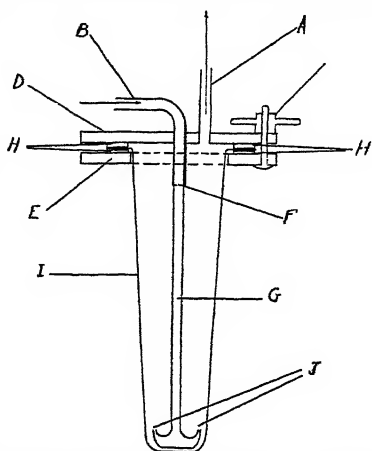


Fig. 8.—Platinum "solution vessel" and connections ( $\frac{1}{2}$  actual dimensions).

A—Outlet tube (brass); B—Inlet tube (brass); C—Thumb-screws (3); D—Cover plate (brass); E—Brass circle; F—Cemented joint; G—Glass tube; H—Rubber washers; I—Platinum vessel; J—Jets (4).

the solution during deëmanation; use of an automatic regulator to maintain constant pressure in the ionization chamber during measurements; maintenance of optimum pressure gradient along air-current line through the measuring apparatus, thus assuring minimum error on account of pressure variations, and maximum speed of measurement; protection of the insulation of the electroscope by means of a current of dry air. Analyses by this method gave results agreeing very well with results obtained by gravimetric methods, and required much less time for each determination.

In concluding, the writer wishes to express his sincere appreciation of the valuable criticisms of Dr. Herbert N. McCoy at whose suggestion this research was taken up.

CHICAGO, ILL.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

## THE HEAT OF FORMATION OF SILVER IODIDE.

BY HUGH STOTT TAYLOR AND WILLIAM THEODORE ANDERSON, JR.

Received March 29, 1921.

A discrepancy, amounting to 600 calories, exists between the determinations of the heat of formation of silver iodide as measured by Jones and Hartmann<sup>1</sup> using electrometric methods and the calorimetric determinations of Braune and Koref.<sup>2</sup> The values obtained are 14,565 and 15,100 calories respectively, so that the divergence represents a difference of some 4% which is much greater than would be anticipated from the reproducibility of either set of experimental measurements. Certain electrometric determinations by Taylor<sup>3</sup> and Perrott, involving the iodides of silver, lead and cadmium, have shown agreement with the calorimetric data of Braune and Koref and favor the adoption of the higher value for the heat of formation of silver iodide.<sup>4</sup>

<sup>1</sup> Jones and Hartmann, *THIS JOURNAL*, 37, 752 (1915).

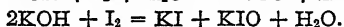
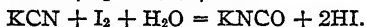
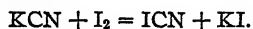
<sup>2</sup> Braune and Koref, *Z. anorg. Chem.*, 87, 175 (1914).

<sup>3</sup> Taylor, *THIS JOURNAL*, 38, 2295 (1916); Taylor and Perrott, *ibid.*, 43, 484 (1921).

<sup>4</sup> Since the communication of the present paper an article by O. Gerth has appeared in *Z. Elektrochem.*, 27, 287 (1921), in which new electrometric measurements of the free energy and heat of formation of silver iodide have been made. By substituting a direct experimental method in place of a calculation of liquid junction potentials in the silver|silver iodide|iodine cells, Gerth has demonstrated that it is in the calculation of such liquid junction potentials that the discrepancy above mentioned has arisen. The value obtained by Gerth for the heat of formation of silver iodide is 15158 calories, in good agreement with the value of 15150 calories obtained by one of us (H. S. T.) at an earlier date. The present communication confirms the correctness of these results and of the earlier calorimetric measurements of Braune and Koref.

The calorimetric data of Braune and Koref were obtained by measurement of the heat evolution (a) when iodine reacted with silver suspended in potassium cyanide solution; (b) when silver iodide dissolved in a similar solution. The difference between the two heat effects was taken to be the heat of formation of silver iodide. A 3 *N* solution of potassium cyanide was employed in the determinations.

Objection to the calorimetric procedure may be urged, owing to the possibility that the iodine may have entered into side reactions with the potassium cyanide solution. Some such possibilities may be illustrated by means of the equations,



If such side reactions occurred, the desired heat of formation would not be obtained unless the presence of metallic silver caused the reduction of all these oxidized compounds. Only in that case would the solution obtained be identical with that resulting from the interaction of silver iodide and potassium cyanide, as in the second part of the calorimetric measurement.

The nature and extent of the various possible side reactions must manifestly depend in part on the concentration of potassium cyanide solution employed in the determination, as well as upon the relative proportions of iodine and potassium cyanide present together during the course of the experiment. With this in mind, a repetition of the calorimetric experiments of Braune and Koref has been undertaken, using, instead of the 3 *N* cyanide solution employed by them, a 1 *N* solution. The modifying effect of dilution made itself at once apparent in the lower values obtained for the heat of solution of silver iodide. This result was to be anticipated, as, in the more dilute solution, complex formation and double decomposition would occur to a less degree. The heat effects obtained from the interaction of the silver and the iodine were, however, also correspondingly lower and, as the subjoined table shows, the net thermal effect obtained for the heat of formation of silver iodide in the more dilute solution is almost exactly that previously obtained by Braune and Koref using the stronger solution of potassium cyanide. We regard this as strong proof of the correctness of the calorimetric determination of the required heat of formation.

### Experimental.

**Apparatus.**—The apparatus used has been recently described by Taylor and Perrott<sup>5</sup> and does not therefore need to be discussed here. The method employed was essentially the same. Instead of measuring the current employed in the electrical heating of the solution for calibration purposes

<sup>5</sup> Taylor and Perrott, *THIS JOURNAL*, 43, 491 (1921).

by means of a coulometer, a measurement of the time of heating was made as well as the voltage drop over a resistance functioning as a heating element. The calibration of this resistance in terms of heating element and lead wires was carefully checked. The total resistance of the heater and leads was 10.35 ohms. The resistance of the heating element alone was 10.17 ohms. The temperature rise of the calorimeter system due to the interaction of a given weight of iodine with silver suspended in the potassium cyanide solution having been observed, the rise in temperature due to the introduction of a measured amount of electrical energy was then determined. This was followed by a measurement of the temperature rise from the solution of a given weight of silver iodide and this by a second measurement of the heat rise due to electrical energy. Thereafter the experiments were conducted in the order indicated in the table. The experiments were conducted at room temperature.

**Materials.**—Finely divided silver was prepared by igniting powdered silver oxide at 400° for several hours. This latter was obtained from high grade silver nitrate by precipitation with alkali followed by a thorough washing to remove excess of alkali and salts.

Resublimed iodine of high grade was used. It was finely powdered in a mortar before use.

The silver iodide employed was obtained by precipitation from solutions of high grade silver nitrate and potassium iodide. It was washed free from soluble salts and with ammonia to remove any possible chloride. The material was dried and used in the amorphous form thus obtained.

Very high grade imported potassium cyanide was employed, 800 cc. of a 1 *N* solution being used in the experiments.

The following table gives the experimental results obtained and the calculated values for the heats of the several reactions.

Expt.	Iodine G.	Rise in temp. °C.	Volts.	Time. Sec.	Rise on heating. °C.	Heat of reaction per mol. iodide, cal.
	3.127	0.710	8.30	480	0.849	25,500
2	2.359	0.533	8.10	300	0.506	25,290
4	2.740	0.695	8.10	360	0.681	25,370
7	3.467	0.877	8.10	360	0.677	25,455
8	1.586	0.393	10.52	120	0.375	25,310
					Mean	25,385
	AgI. G.					
3	5.336	0.276	8.10	180	0.319	10,215
5	6.077	0.323	8.10	180	0.328	10,200
6	7.131	0.380	8.10	180	0.330	10,340
					Mean	10,251

The difference in value of the two mean heat effects with iodine and silver iodide gives the desired heat of reaction  $\text{Ag} + \text{I} = \text{AgI} + (25385 - 10251)$  calories; whence  $Q = 15,134$  calories. In 3 *N* potassium cyanide solution the value obtained by Braune and Koref was 15,100 calories. Since



the latter used crystallized silver iodide it is evident that the divergence between the two is within the error of the measurement.

### Summary.

A repetition of Braune and Koref's calorimetric measurement of the heat of formation of silver iodide using 1 *N* potassium cyanide instead of 3 *N* solution as solvent for silver iodide has been made. Their result, a value of 15,100 calories per mole of silver iodide, has been confirmed.

PRINCETON, NEW JERSEY.

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[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, COLUMBIA UNIVERSITY, No. 373.]

## THE CATALYTIC INFLUENCE OF FOREIGN OXIDES ON THE DECOMPOSITION OF SILVER OXIDE, MERCURIC OXIDE AND BARIUM PEROXIDE.<sup>1</sup>

BY JAMES KENDALL AND FRANCIS J. FUCHS.

Received May 13, 1921.

### Introduction.

The results obtained by previous investigators on the decomposition of substances liberating oxygen are, for the most part, very indefinite and unsatisfactory. Particular reference may be made to the extensive work done on the decomposition of *potassium chlorate* under the catalytic influence of metallic oxides.<sup>2</sup> The decomposition temperatures recorded for *simple oxides* also vary widely.

	°C.		°C.		°C.
Ag <sub>2</sub> O	250-350	BaO <sub>2</sub>	450-825	CrO <sub>3</sub>	180-320
HgO	175-660	MnO <sub>2</sub>	210-560	CuO	800-1200

The data for *mixtures of oxides* are, in general, still more divergent. It is often impossible to correlate the results of different observers, either because the relative amounts of the components are not specified at all or because mention is made in such a way as to leave it quite uncertain whether volume, weight or molecular composition units were employed.

The present investigation is an attempt to obtain systematic data on the dissociation equilibria of silver oxide, mercuric oxide and barium peroxide, as affected by the presence of other oxides. The choice of these three oxides as experimental material was made on account of their ease of preparation and their conveniently low decomposition temperatures. It was anticipated that the results would prove of interest not only with respect to the mechanism of the reactions actually studied, but

<sup>1</sup> Condensation of a thesis submitted by Francis J. Fuchs in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, May 1920.

<sup>2</sup> See Sodeau, *J. Chem. Soc.*, 81, 1067 (1902).

also in connection with the more general problems of heterogeneous catalysis<sup>3</sup> and the action of promoters.<sup>4</sup> The data for barium peroxide, finally, are of particular importance in view of the possibility of their application to the industrial revival of the Brin process.

The results of earlier work on the dissociation of the above oxides may first be summarized.

#### Previous Work.

**Silver Oxide.**—No direct determinations of oxygen dissociation pressures below 300° have been made, although many investigators<sup>5</sup> claim that decomposition begins even below 200°. G. N. Lewis<sup>6</sup> found equilibrium pressures of 20.5 atmospheres at 302°, 32 atmospheres at 325° and 207 atmospheres at 445°. Oxygen evolution proceeded very slowly at first, but the accumulation of finely divided silver in intimate admixture with the oxide accelerated its decomposition considerably. Finely divided platinum and manganese dioxide were also shown to catalyze the reaction. To explain these results, Lewis suggested that the decomposition of the oxide takes place in two stages: (1)  $\text{Ag}_2\text{O} \rightarrow 2\text{Ag} + \text{O}$ ; (2)  $2\text{O} \rightarrow \text{O}_2$ . The slowness of the latter reaction controls the velocity of the decomposition and on finely divided surfaces the adsorbed gases may be expected to react much more rapidly.

**Mercuric Oxide.**—The oxygen dissociation pressures above 500° were first established by Pélabon<sup>7</sup> and the curve has been extended below 500° by Taylor and Hulett.<sup>8</sup> These latter investigators also examined the effect of finely divided platinum and certain metallic oxides upon the reaction, and found that while the rate of oxygen evolution was considerably increased, the equilibrium pressure was not significantly changed. The temperature at which the oxygen pressure equals 1 atmosphere is approximately 490° according to Pélabon, and 500° according to Taylor and Hulett. No difference in behavior between the yellow and the red modifications of mercuric oxide was obtained.

**Barium Peroxide.**—Hildebrand,<sup>9</sup> in a careful investigation on the thermal dissociation of barium peroxide, showed that solid solutions between  $\text{BaO}$  and  $\text{BaO}_2$  are formed, the oxygen pressure of the two saturated solutions reaching 1 atmosphere at approximately 825°. Le Chatelier<sup>10</sup> obtained a lower value, 796°. The difference is probably due to the influence of traces of water upon the reaction.

Extensive work on the effect of other oxides on the decomposition of barium peroxide has recently been carried out by Hedvall.<sup>11</sup> Nearly all of the oxides tested re-

<sup>3</sup> H. S. Taylor, *J. Ind. Eng. Chem.*, **13**, 75 (1921).

<sup>4</sup> Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

<sup>5</sup> For example, Le Chatelier, *Bull. soc. chim.*, [2] **48**, 342 (1887).

<sup>6</sup> G. N. Lewis, *Z. physik. Chem.*, **52**, 310 (1905); **55**, 449 (1906); *THIS JOURNAL*, **28**, 139 (1906).

<sup>7</sup> Pélabon, *Compt. rend.*, **128**, 625 (1899). Earlier experimenters obtained very discordant results.

<sup>8</sup> Taylor and Hulett, *J. Phys. Chem.*, **17**, 565 (1913).

<sup>9</sup> Hildebrand, *THIS JOURNAL*, **34**, 246 (1912).

<sup>10</sup> Le Chatelier, *Compt. rend.*, **115**, 659 (1892).

<sup>11</sup> Hedvall, *Z. anorg. Chem.*, **104**, 163 (1918); **108**, 119 (1919). These papers were not published until the present work was well under way. Some duplication of experiments consequently occurs, but in view of the different methods employed this is in a certain measure desirable, since it offers a good means of testing the reliability of the results obtained.

duced the decomposition temperature and increased the rate of oxygen evolution considerably. In some cases (for example, with cuprous oxide) high reaction velocities were found even at temperatures below 200°. With certain oxides the effect was considered to be purely catalytic, with others formation of a compound between barium oxide and the added oxide was indicated.

**General Review.**—In few of the above investigations do the results of different workers stand direct comparison, and it is obvious that the chief cause of the discrepancies is the variable physical condition of the materials used. No doubt exists that the reactivity of a solid phase is very considerably controlled by its previous history,<sup>12</sup> and it is futile to expect a strongly ignited oxide to show the same behavior as a sample freshly precipitated from aqueous solutions and dried at a low temperature.

In all of the present work, consequently, standard and reproducible methods of preparation have been adopted. The various oxides were obtained in a finely divided state by precipitation whenever possible, and dried first in a vacuum desiccator and then in a Freas oven regulated to 140°. All oxides were dried for at least two months before use. In the event of their not attaining constant weight within that period, it was necessary to remove the last traces of firmly retained moisture by ignition. This procedure was not adopted except as a last resort, since it is evident from the literature that extreme and prolonged ignition renders the oxides more or less inert. Some investigators have claimed that non-ignited samples do not give reliable results (possibly owing to adsorbed gases or traces of water), but the data here presented do not substantiate this view, as will be seen below.

### Experimental.

It must be noted at the start that the aim of the present work is to secure a preliminary survey over a comparatively wide field rather than to obtain results of the highest accuracy for a few isolated systems.<sup>13</sup> For each of the fixed oxides examined, and for each of the mixtures of these with other oxides, the decomposition temperature has been determined at a single pressure only, namely 1 atmosphere. Variations in the barometer were found not to affect the temperature beyond the limits of experimental error.

The compositions of all mixtures are expressed in molecular percentages. Mixture of the component oxides was accomplished by mechanical agi-

<sup>12</sup> See Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan Co., 1919, p. 16.

<sup>13</sup> It is planned to examine certain of the more interesting systems in greater detail in a subsequent investigation.

tation.<sup>14</sup> That this was adequate to ensure intimate admixture was proved by comparing the results so obtained with those given by co-precipitated oxides in the case of the system silver oxide:mercuric oxide. The decomposition temperatures checked throughout within the limits of experimental error. That the temperatures determined are true equilibrium temperatures for an oxygen pressure of 1 atmosphere was established for each mixture by approaching the equilibrium point from both directions, *i. e.*, with rising and with falling temperature. Reproducible values, within experimental errors, were consistently obtained. In certain cases a slight difference apparently existent on first trial between the values recorded for rising and for falling temperatures was found on further examination to be due to the slowness with which equilibrium was attained. By decreasing the rate of temperature change, such differences could be proportionately diminished until they became, to all intents and purposes, negligible.

**Description of Apparatus.**—The apparatus used is shown in the accompanying diagram (Fig. 1.) The furnace was of the crucible type (Hoskins make), the interior heating chamber being cylindrical, 12.5 cm. in diameter and 12.5cm. deep. A special

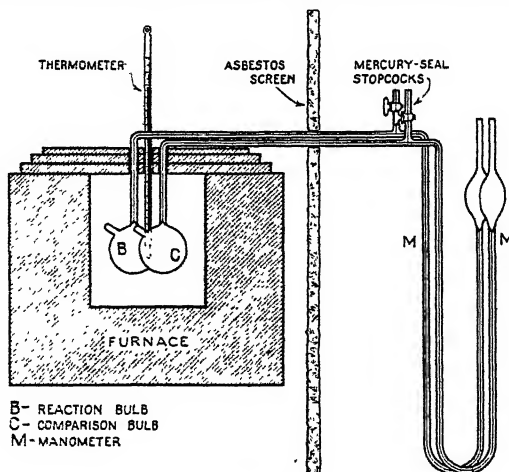


Fig. 1.

heating coil and rheostat capable of maintaining a constant temperature at any point up to 500° were employed. Temperatures were indicated on a nitrogen-filled thermometer<sup>15</sup> of the Tycos type, reading to 500° and graduated for 75mm. immersion.

<sup>14</sup> The separate oxides were first ground in a mortar to break up any caked masses. Every oxide employed was thus reduced to an approximate fineness of 100 to 200 mesh before use. The two oxides were then shaken up together in a closed test-tube until the mixture was apparently uniform. This was followed by a second light grinding in a mortar, after which the mixture was again thoroughly shaken.

<sup>15</sup> The decomposition temperatures obtained were, in general, higher than was expected when the investigation was commenced. It is recognized that in many systems,

The bulb of the thermometer consequently occupied the central position in the heating chamber.<sup>16</sup> The thermometer was calibrated while in position at the usual fixed points, and the standardization checked at intervals throughout the work.

The oxides under examination were enclosed in a thin-walled bulb of Jena glass, 25 mm. in diameter, joined to a capillary stem. The mixture was introduced into this reaction bulb through a short side tube, which was then sealed off. The extension of the capillary stem was bent, as indicated in the figure, to form a manometer, a mercury-seal stopcock for evacuating and charging with oxygen being also attached as shown. Benzyl benzoate (an inert, non-hygroscopic, non-volatile liquid of low density) was employed as manometer liquid, its movement on an attached millimeter scale being observed through a lens. An asbestos screen prevented radiation of heat from the furnace to the manometer.

A comparison bulb, with a blank charge of silica and a free volume as nearly as possible equal to that of the reaction bulb, was placed directly beside it in the heating chamber. This comparison bulb was attached to a second manometer, exactly similar to the first. Both bulbs were very carefully cleaned and dried before use.

**Manipulation.**—Before a determination was begun the two charged bulbs (already in position in the furnace) were filled with pure oxygen under atmospheric pressure through the stopcocks, and the benzyl benzoate in the two manometers adjusted to the same level. The temperature of the furnace was then raised very slowly and uniformly, and the change in level of the manometers noted. So long as nothing occurred in the reaction bulb, both liquid columns moved at uniform rates owing to the expansion of the enclosed oxygen. The ratio of these rates (very nearly unity, since the free volumes of the two bulbs were made as nearly equal as possible) was carefully established. As an arbitrary standard of unit volume change, a rise of 10 mm. in the comparison-bulb manometer (corresponding to a temperature change of approximately 2°) was fixed upon. As often as this unit volume change was indicated, the two stopcocks were opened to bring the systems back to atmospheric pressure, the temperature rising very gradually all the time.

Readings were continued in this way until the reaction-bulb manometer showed an abnormal volume change, indicating that evolution of oxygen had begun. The temperature was still allowed to rise slowly for about 50°, and the "rate of decomposition" arbitrarily measured by comparing the movements of the two columns. The current was then reduced where the curves are above 300° throughout, a thermocouple would have afforded a more convenient and accurate method of temperature measurement. In view of the inadvisability of changing the method when half-way through the work, however, the original set-up was retained.

<sup>16</sup> The uniformity and constancy of temperature within the heating chamber were carefully tested. It was found that while a small temperature gradient existed at different heights, yet the temperature at different points near the center of the chamber remained constant and uniform, well within the experimental limits of accuracy, over extended periods of time. For very accurate determinations, a liquid bath would of course be preferable, but for the present work the air-bath here employed proved perfectly satisfactory.

sufficiently to cool the furnace gradually. Oxygen continued to be evolved for some time, as could be seen from the opposed volume changes in the two manometers, but as the temperature slowly fell a normal contraction was finally established in the reaction bulb. The temperature at which this first occurred was noted and compared with that at which oxygen evolution commenced. After the technique of the method had been mastered, these two temperatures in any single determination rarely varied by more than  $2^{\circ}$  to  $5^{\circ}$ . The experiment was repeated with new charges of oxides and with varying rates of heating and cooling until the equilibrium point had been satisfactorily fixed.

The results obtained for the various systems examined may now be presented. The first series, in which the decomposition of silver oxide is studied, is taken up somewhat in detail in order to make clear, certain points in the experimental procedure. The remaining systems are more briefly reported upon and subjected to a general discussion later.

#### The System $\text{Ag}_2\text{O} : \text{HgO}$ .

*Silver oxide* was prepared by addition of a saturated solution of barium hydroxide to a warm solution of recrystallized silver nitrate in distilled water free from carbon dioxide. The precipitate was washed until free from barium hydroxide and nitrate, then carefully dried. Particular precautions were taken to prevent absorption of carbon dioxide at any stage of the preparation.

*Mercuric oxide* was obtained in a similar way by precipitation from hot solutions of mercuric chloride and barium hydroxide. The red precipitate was repeatedly digested with boiling water, filtered under suction and carefully dried.

Ag <sub>2</sub> O in mixture. %.	Equilibrium Temperature ( $p_{\text{O}_2} = 1 \text{ atm.}$ ).			Relative rate of decomposition. $304^{\circ}$ .
	Rising. °C.	Falling. °C.	Mean. °C.	
100	254	254	254	1.0
90	245	245	245	2.0
50	231	230	231	7.0
10	249	250	250	10.0
0	429	432	431	....

The first column in the above table shows the molecular composition of the oxide mixtures used. The average decomposition temperatures for 1 atmosphere of oxygen, as obtained with rising and with falling temperature, follow. The mean of all results obtained is given in the fourth column. The last column indicates the catalytic influence of the added oxide (mercuric oxide) on the decomposition of the silver oxide at a fixed temperature,  $304^{\circ}$  ( $50^{\circ}$  above the decomposition temperature of pure silver oxide). These relative decomposition rates were obtained by directly comparing the excess movements in the manometer levels for reaction bulbs containing the pure oxide and the different mixtures at this temperature, correcting for the various amounts of silver oxide present in each bulb.

The results obtained for pure silver oxide were in agreement with those of G. N. Lewis.<sup>6</sup> When the oxide was first heated, oxygen evolution was extremely slow below  $300^{\circ}$ ; above this temperature it became increasingly more rapid. On subsequent heatings, decomposition was markedly

accelerated by the traces of finely divided silver already present.<sup>17</sup> The results here given all refer to fresh samples of oxide. Although it was necessary to perform the work with great care in order to obtain concordant results, the samples used were evidently more reactive than Lewis's preparations. We are perfectly confident, from the regularity of the results, that the temperatures given above are true "oxygen equilibrium temperatures" and that the volume changes indicated in the manometer cannot be ascribed to evolution or absorption of minute traces of water or carbon dioxide present in the oxide. Direct tests showed that exceedingly small additions of water or carbon dioxide to the oxide mixtures produced very large and irregular volume changes, the vaporization of 0.0001 g. of water involving a depression of approximately 150 mm. on the manometer scale. In none of the measurements recorded in this article was any such effect observed.

Pure mercuric oxide also showed a very small decomposition rate, which is independent, however, of the period of heating. The decomposition temperature obtained for  $p_{O_2} = 1$  atmosphere is much lower than that recorded by previous investigators, probably owing to the different methods of preparation employed.

The results for mixtures of the two oxides were more easily established. As will be seen from the figures in the final column, the decomposition temperature of silver oxide is lowered and the rate of oxygen evolution considerably increased in the presence of mercuric oxide. A series of measurements with "co-precipitated oxides" in the same proportions (obtained by adding barium hydroxide solution to a solution containing the requisite amounts of silver nitrate and mercuric chloride) gave substantially identical results, the actual mean temperatures obtained being 246°, 232° and 251° for the three mixtures tabulated above.

#### The System $Ag_2O : BaO_2$ .

*Barium peroxide* was prepared from recrystallized barium chloride by addition of sodium peroxide, the two solutions being mixed at 0° under constant stirring. The precipitated octohydrate was filtered, washed thoroughly and dehydrated by heating first to 100°, then (after standing in a vacuum desiccator over phosphorus pentoxide for two weeks) to 350°, the heating being very carefully conducted in order to ensure a slow rise in temperature and prevent formation of barium hydroxide.

Ag <sub>2</sub> O in mixture. %.	Equilibrium Temperature ( $p_{O_2} = 1$ atm.).			Relative rate of decomposition. 304°.
	Rising. °C.	Falling. °C.	Mean. °C.	
90	201	200	201	>4.0
50	200	198	199	>7.5
10	226	226	226	>15.0

As in the previous system, the decomposition temperature of silver oxide is lowered and the rate of decomposition markedly increased by the second oxide present. Here

<sup>17</sup> For one sample, for example, the decomposition rates at 304° for three successive heatings were 1:3:6.

the oxygen evolution from mixtures of the two oxides at the fixed temperature  $304^{\circ}$  was so rapid as to carry the manometer liquid beyond the bend of the tube. The values given above are consequently merely minima.

#### The System $\text{Ag}_2\text{O} : \text{CuO}$ .

*Copper oxide* was prepared by slow addition of 10% sodium hydroxide solution to a hot solution of carefully purified cupric sulfate. The precipitate, when completely transformed from bluish to deep black, was separated and repeatedly digested with boiling water until free from sulfate. It was then dried by heating first to  $100^{\circ}$ , then to  $280^{\circ}$ .

Ag <sub>2</sub> O in mixture. %.	Equilibrium Temperature ( $p_{\text{O}_2} = 1 \text{ atm.}$ ).			Relative rate of decomposition. $304^{\circ}$ .
	Rising. °C.	Falling. °C.	Mean. °C.	
90	249	249	249	> 3.0
50	240	241	240	> 8.0
10	249	250	250	> 50.0

In this system the temperature of decomposition of the silver oxide ( $254^{\circ}$ ) is not significantly affected; the rate of oxygen evolution, however, is enormously increased.

To test the effect of the previous history of the added oxide on the temperature and rate of the decomposition, the experiments for the equimolecular mixture were repeated with cupric oxide which had previously been ignited to a red heat several times.<sup>18</sup> The relative inactivity of such a specimen was shown by the fact that the equilibrium temperature was changed to  $252^{\circ}$ , the rate of oxygen evolution also falling off considerably.<sup>19</sup>

#### The System $\text{Ag}_2\text{O} : \text{MnO}_2$ .

*Manganese dioxide* was prepared by adding potassium chlorate in small quantities to a boiling, slightly acid solution of recrystallized manganese nitrate. The precipitate was separated off, washed repeatedly and dried first at  $100^{\circ}$  and then at  $300^{\circ}$  in an atmosphere of oxygen.

Ag <sub>2</sub> O in mixture. %.	Equilibrium Temperature ( $p_{\text{O}_2} = 1 \text{ atm.}$ ).			Relative rate of decomposition. $304^{\circ}$ .
	Rising. °C.	Falling. °C.	Mean. °C.	
90	220	220	220	> 4.0
50	229	231	230	> 4.0
10	271	272	271	10.0
0	418	420	419	...

For the 90% and 50% mixtures, the usual phenomena (lowering of decomposition temperature and increase in rate of decomposition) are again encountered. For the 10% mixture, however, although the rate of oxygen evolution at  $304^{\circ}$  is apparently greater than that of pure silver oxide, the actual equilibrium temperature is raised.

Pure manganese dioxide is found to have a definite decomposition temperature of  $419^{\circ}$ ; the rate of decomposition at that point is slow, but becomes much more rapid above  $480^{\circ}$ . Previous experimenters have obtained very discordant values for this oxide. Moissan<sup>20</sup> gives  $230^{\circ}$ ; Wright and Luff,<sup>21</sup>  $390^{\circ}$ ; Gorgen,<sup>22</sup>  $400^{\circ}$ ; Hempel,<sup>23</sup>  $470^{\circ}$

<sup>18</sup> The dissociation temperature of  $\text{CuO}$  was found by Foote and Smith, *THIS JOURNAL*, 30, 1344 (1908), to be about  $1025^{\circ}$ .

<sup>19</sup> Compare Lemoine, *Compt. rend.*, 162, 702 (1916).

<sup>20</sup> Moissan, *Ann. chim. phys.*, 21, 232 (1880).

<sup>21</sup> Wright and Luff, *Ber.*, 11, 2144 (1878).

<sup>22</sup> Gorgen, *Compt. rend.*, 110, 134 (1890).

<sup>23</sup> Hempel, *Z. Elektrochem.*, 18, 729 (1912).



to 500°; while Meyer and Rötgers<sup>24</sup> state that no dissociation is observable below 530° in air or below 565° in pure oxygen. These discrepancies are undoubtedly due to differences in the physical condition and in the completeness of the dehydration of the oxide.

#### The System $\text{Ag}_2\text{O} : \text{Fe}_2\text{O}_3$ .

*Ferric oxide* was prepared by addition of excess of ammonium hydroxide to a clear solution of recrystallized ferric chloride. The precipitate was digested with boiling water several times until free from chloride, dried by heating to 100° and finally dehydrated by ignition in a porcelain crucible.

Ag <sub>2</sub> O in mixture. %.	Equilibrium Temperature ( $p_{\text{O}_2} = 1 \text{ atm.}$ ).			Relative rate of decomposition. 304°.
	Rising. ° C.	Falling. ° C.	Mean. ° C.	
90	222	224	223	> 2.5
50	247	248	248	> 5.0
10	270	268	269	> 10.0

The results are very similar to those obtained with manganese dioxide in the preceding table.

#### The System $\text{Ag}_2\text{O} : \text{CeO}_2$ .

*Cerium dioxide* was prepared by addition of ammonium hydroxide to a solution of purified ceric nitrate. The precipitate was thoroughly washed, dried at 100°, then very slowly raised to a red heat to complete the dehydration.

Ag <sub>2</sub> O in mixture. %.	Equilibrium Temperature ( $p_{\text{O}_2} = 1 \text{ atm.}$ ).			Relative rate of decomposition. 304°.
	Rising. ° C.	Falling. ° C.	Mean. ° C.	
90	248	250	249	1.0
50	269	273	271	1.5
10	280	280	280	4.5

In this series the catalytic influence of the added oxide upon the decomposition of the silver oxide is still less pronounced than in the cases of manganese dioxide and ferric oxide. The 90% mixture gives a decomposition temperature only slightly below that of pure silver oxide, while the decomposition temperatures for the remaining mixtures are considerably higher. The rate of oxygen evolution for the various mixtures at 304° is less than in any of the previous series.

#### The System $\text{Ag}_2\text{O} : \text{SiO}_2$ .

*Silicon dioxide* was obtained by addition of hydrochloric acid to a solution of sodium silicate. The gelatinous precipitate was washed, ignited to a powder, washed repeatedly till free from salts, dried and re-ignited.

Ag <sub>2</sub> O in mixture. %.	Equilibrium Temperature ( $p_{\text{O}_2} = 1 \text{ atm.}$ ).			Relative rate of decomposition. 304°.
	Rising. ° C.	Falling. ° C.	Mean. ° C.	
90	250	251	250	1.5
50	261	263	262	2.0
10	285	284	284	5.0

The results are substantially identical with those given by cerium dioxide mixtures.

#### The System $\text{Ag}_2\text{O} : \text{CrO}_3$ .

*Chromic anhydride* was prepared by careful addition of conc. sulfuric acid to a well-stirred solution of recrystallized sodium dichromate. The precipitated chromium trioxide was separated by filtering through glass wool, washed with conc. nitric acid

<sup>24</sup> Meyer and Rötgers, *Z. anorg. Chem.*, 57, 104 (1908). See however, Askenasy and Klonowski, *Z. Elektrochem.*, 16, 107 (1910).

until free from sulfate, dried as completely as possible on a porous tile and finally heated to constant weight at 120°.

The decomposition temperatures for pure chromium trioxide given in the literature vary widely. Arctowski,<sup>25</sup> for example, claims that rapid decomposition occurs just above the melting point (180–190°), while Honda<sup>26</sup> has more recently reported a *minimum* temperature of 320°, the resultant lower oxide having the composition Cr<sub>6</sub>O<sub>15</sub>. The present experiments indicated melting of the oxide at 180° and an equilibrium temperature for  $p_{O_2} = 1$  atmosphere at 190°. Owing to the volume change involved in the change of state the manometer readings were difficult to interpret unless the temperature was varied extremely slowly. The above values are to be regarded as only approximate.

With mixtures of chromium trioxide and silver oxide containing 90% and 50% silver oxide no concordant results could be obtained. After the melting of the chromium trioxide around 180° rapid oxygen evolution was noted at about 200° with rising temperature, but with falling temperature decomposition ceased at much higher points, 225° and 245° respectively. The mixture containing 10% of silver oxide, however, gave a definite equilibrium temperature of 161°, *i. e.*, below the melting-point of chromium trioxide.

#### Mercuric Oxide Systems.

Added oxide.	HgO in mixture, %.	Equilibrium Temperature ( $p_{O_2} = 1$ atm.).			Relative rate of decomposition. 471°.
		Rising. ° C.	Falling. ° C.	Mean. ° C.	
	100	429	432	431	1.0
CuO	90	398	400	399	> 1.0
	50	380	382	381	> 2.0
	10	419	419	419	> 10.0
BaO <sub>2</sub>	90	279	281	280	> 1.0
	50	278	276	277	> 1.5
	10	282	284	283	> 7.0
MnO <sub>2</sub>	90	369	371	370	> 1.0
	50	225	224	225	> 1.5
	10	354(?)	380(?)	367(?)	> 10.0
Fe <sub>2</sub> O <sub>3</sub>	90	399	399	399	> 1.5
	50	410	411	410	> 5.0
	10	425	423	424	> 20.0
CeO <sub>2</sub>	90	414	414	414	> 2.0
	50	430	431	431	> 2.0
	10	439	439	439	> 5.0

As in the case of silver oxide systems, copper oxide and barium peroxide both lower the decomposition temperature and increase the rate of oxygen evolution.<sup>27</sup> Copper oxide, as before, has the greater effect upon the rate of the reaction, barium peroxide the greater effect on the equilibrium temperature.

Ferric oxide and cerium dioxide again exhibit much less pronounced influence, the decomposition temperature being only slightly changed. Manganese dioxide here induces a far greater temperature decrease. The results for the 10% mixture, however, are rather uncertain.

<sup>25</sup> Arctowski, *Z. anorg. chem.*, 9, 29 (1895).

<sup>26</sup> Honda, *Science Repts. Tohoku Imp. Univ.*, 4, 897 (1915).

<sup>27</sup> A reference temperature of 471° (40° above the decomposition point of pure HgO) has been chosen for comparing rates of reaction in the above table.

Attempts were also made to examine the effect of chromic anhydride and silicon dioxide on the decomposition of mercuric oxide. With chromic anhydride, phenomena similar to those described in the silver oxide series were observed. The 90% and 50% mixtures showed rapid evolution with rising temperature immediately after fusion of the chromium trioxide, *i. e.*, below 200°. With falling temperature, decomposition ceased at much higher temperatures. The 10% mixture gave a definite equilibrium temperature of 171°.

With silicon dioxide no satisfactory results could be obtained. The 90% mixture evolves oxygen at a temperature slightly below the normal, while with the remaining mixtures, the decomposition temperature is considerably raised. No consistency could be attained, however, between results with rising and with falling temperatures.

#### Barium Peroxide Systems.

Added oxide.	BaO <sub>2</sub> in mixture. %.	Equilibrium Temperature. ( $p_{O_2}$ = 1 atm.).		
		Rising. °C.	Falling. °C.	Mean. °C.
CuO	90	317	320	318
	50	322	322	322
	10	328	329	329
MnO <sub>2</sub>	90	342	342	342
	50	322	326	324
	10	330(?)	337(?)	333(?)
Fe <sub>2</sub> O <sub>3</sub>	90	321	324	323
	50	345	344	345
	10	357(?)	360(?)	358(?)

The equilibrium temperature for pure barium peroxide (approx. 825°) being far beyond the limits of the present work, no column of relative rates of decomposition can be included in the above table. For all of the mixtures listed, however, the rate of oxygen evolution even below 400° was already quite rapid, so that the catalytic effect of the added oxides upon the reaction is in all cases very considerable.

The presence of copper oxide, manganese dioxide or ferric oxide lowers the decomposition temperature of barium peroxide by nearly 500°. With the 10% mixtures of the last two oxides, the results obtained were not altogether satisfactory, the figures given above being the mean of several rather divergent determinations.

With cerium dioxide mixtures, no indications of oxygen evolution were given at 520°, the limit of temperature measurement.

In the presence of silicon dioxide, decomposition of the barium peroxide was found to begin at much lower temperatures. With rising temperature, values of 247°, 295° and 309° were obtained for mixtures containing 90%, 50% and 10% of barium dioxide respectively. With falling temperature, however, these figures could not be duplicated.

#### Discussion of Results.

**Silver Oxide Systems.**—From the tables given above, it is evident that the decomposition temperature of silver oxide for  $p_{O_2}$  = 1 atmosphere is very markedly affected by the presence of other oxides. In all cases the first addition of a foreign oxide lowers the decomposition temperature. With larger amounts a minimum value is reached, while an excess of added oxide may actually raise the decomposition temperature above the normal. Invariably, however, the rate of oxygen evolution is increased.

If we are to retain the view that a catalyst, however much it may hasten

the attainment of equilibrium, cannot alter the equilibrium point of a reaction, then it is certain that the influence of the foreign oxides throughout this series is not purely catalytic, since the equilibrium point is undoubtedly changed. The increase in the rate of oxygen evolution may it is true, be ascribed entirely to adsorption effects, as indicated by Lewis,<sup>6</sup> but the wide variations in the decomposition temperature cannot be satisfactorily explained on the basis of adsorption alone. All of the results, indeed, point to the conclusion that the added oxide enters directly into the reaction.

The simplest and most plausible assumption that can be made is the formation of transient intermediate compounds between the two oxides.<sup>28</sup> Such compounds could be regarded as *salts* produced by the combination of a basic and an acidic component, and the relative instability of the salt would determine the change in the decomposition temperature. Silver oxide being characteristically basic, we might expect other basic oxides to give very unstable complexes with it. In point of fact, the decomposition temperature is lowered most considerably by barium dioxide and mercuric oxide. The complexes of silver oxide and more acidic oxides, on the other hand, might be predicted to be more stable. In line with this, we find excess of ferric, manganese, ceric and silicic oxides raising the decomposition temperature.

In the system  $\text{Ag}_2\text{O}:\text{CrO}_3$ , the formation of a salt ( $\text{Ag}_2\text{CrO}_4$ ) between the two components may be definitely established. The salt is produced in the reaction bulb just above the melting point of chromium trioxide with considerable evolution of heat and partial decomposition. With falling temperature, oxygen evolution ceases at much higher temperatures, indicating that the complex is more stable than chromium trioxide. It is still, however, slightly less stable than silver oxide.

**Mercuric Oxide Systems.**—The results for this series are substantially similar to those given by the corresponding silver oxide systems, and the same explanation may be adduced. Barium dioxide lowers the decomposition temperature very considerably, cupric oxide has less effect, ferric and ceric oxides have very little influence upon the equilibrium point. The results for chromium trioxide mixtures point to the formation of a relatively stable compound, mercuric chromate,  $\text{HgCrO}_4$ . In the same way the discordant results for silicon dioxide mixtures with rising and falling temperatures may be explained by the production of mercury metasilicate,  $\text{HgSiO}_3$ .

It is important to note that the results here obtained are in direct opposition to those of G. B. Taylor and Hulett.<sup>8</sup> The only explanation that

<sup>28</sup> Compare Lewis, "A System of Physical Chemistry," Longmans, Green and Co., 1918, vol. 1, p. 456. The formation of solid solutions might affect the results in isolated systems, but could scarcely be adduced as a general phenomenon.

can be suggested at present is that the oxides employed by these investigators were rendered inactive by previous prolonged ignition.

**Barium Peroxide Systems.**—The three oxides listed (cupric oxide, manganese dioxide and ferric oxide) all lower the decomposition temperature nearly  $500^{\circ}$ . If, as appears probable from the results of Hedvall and Zweigbergk,<sup>29</sup> barium dioxide evolves oxygen simultaneously with silver oxide and mercuric oxide in its mixtures with these two oxides, then in their presence its decomposition temperature is still further decreased. Cerium dioxide is much less active. The results for silicon dioxide mixtures are, as before, best explained by the formation of a stable silicate.

Hedvall and Zweigbergk have already obtained evidence in favor of the assumption that, in the majority of systems containing barium dioxide and a foreign oxide, salt formation is the predominant factor in controlling the decomposition. The present results are in general agreement with their data. Quantitative agreement is hardly to be expected in view of the different methods of treatment of the oxides employed. There is, besides, no evidence that the values given by Hedvall and Zweigbergk (as obtained by the determination of breaks in the heating curve) represent true equilibria. In all probability the decomposition temperatures recorded are, in general, too high.

**General Review.**—A mixture of two substances, each of which evolves oxygen when heated alone, almost always decomposes much more readily than either of its separate components. In certain cases each substance simultaneously promotes the decomposition of the other. Silver oxide and hydrogen dioxide, for example, mutually decompose one another at ordinary temperatures.<sup>30</sup> In other instances only one of the components loses oxygen. Thus the decomposition temperature of potassium chlorate is very considerably lowered by the presence of foreign oxides, the case of manganese dioxide being the most familiar. The mechanism of this reaction has been the subject of much speculation. From the work of Sodeau<sup>31</sup> it has been definitely established that the manganese dioxide must enter directly into the decomposition cycle, since a crystalline sample is transformed into a finely-divided powder in the course of the reaction.

Much of the work on the catalytic effect of foreign oxides on the de-

<sup>29</sup> Hedvall and Zweigbergk, *Z. anorg. Chem.*, **108**, 119 (1919). A convenient summary of the results obtained by these workers may be found in *Ann. Repts. Chem. Soc.*, **17**, 40 (1920).

<sup>30</sup> Various theories have been advanced to explain this reaction, Liveing's hypothesis of local energy transfer being particularly interesting. (See Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan Co., 1919, p. 42. The action of other oxides on  $H_2O_2$  has recently been investigated by Loemine (*Compt. rend.*, **162**, 702 (1916)).

<sup>31</sup> Sodeau, *J. Chem. Soc.* **77**, 137, 717 (1900); **79**, 247, 939 (1901); **81**, 1066 (1902).

composition of potassium chlorate is open to question (contradiction between the results of different investigators being frequent) yet a survey of the more reliable data shows that those oxides which have been found to be most active in the present work are also most active in promoting the decomposition of potassium chlorate and hydrogen dioxide. Our knowledge of the whole subject of heterogeneous catalysis is still so elementary that it is dangerous to attempt to draw any final conclusions as to the part which the added oxides play in these processes. For the several series of systems here studied, however, the hypothesis of the formation of intermediate complexes would appear to provide a logical explanation of the experimental facts. In any quantitative study of the rate of decomposition in any particular mixture, of course, adsorption effects would also need to be taken into consideration.

In a subsequent article the practical application of the results obtained for barium dioxide systems to the Brin oxygen process will be discussed, and the effect of the simultaneous addition of more than one foreign oxide upon the temperature and rate of the decomposition investigated. In certain other reactions (*e. g.*, the oxidation of carbon monoxide to the dioxide in the purification of hydrogen<sup>32</sup>) it has been discovered that an enormous increase in the catalytic activity of a single oxide may be induced by the presence of a very small amount of a second oxide which alone may be relatively inert. In the removal of carbon monoxide as a toxic gas from air, similarly, it has been found<sup>33</sup> that mixtures of oxides (*e. g.*,  $\text{MnO}_2$ ,  $\text{CuO}$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Ag}_2\text{O}$ ) are much more efficient than any single component. If this "promoter action" is similarly pronounced in the decompositions here studied (and preliminary experiments indicate that this is the case) then the fascinating possibility arises of resurrecting the Brin process industrially by carrying out the whole cycle of operations at ordinary temperatures. Whether this is feasible in practice remains, of course, to be tested.

### Summary.

The effect of foreign oxides upon the temperature and rate of decomposition of silver oxide, mercuric oxide and barium peroxide under an oxygen pressure of one atmosphere has been experimentally investigated.

In almost all of the systems examined, the added oxide induces a considerable change in the decomposition temperature. Most commonly there is a marked lowering in this point, thus (to cite an extreme case) an equimolecular mixture of barium dioxide and cupric oxide has an oxygen equilibrium pressure of 1 atmosphere at  $322^\circ$ , approximately  $500^\circ$  below the decomposition temperature of pure barium dioxide. In a few systems a

<sup>32</sup> Rideal and Taylor, *op. cit.*, p. 29 *et seq.*

<sup>33</sup> Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, 12, 213 (1920).

comparatively small rise in the decomposition temperature is indicated. In all instances, however, the rate of oxygen evolution is significantly increased.

It must be emphasized that the decomposition temperatures recorded refer to true equilibrium conditions, concordant values being obtained with rising and with falling temperature. Disagreement with the results of previous investigators is, in certain systems, very evident. Much of the earlier work in this field is, however, not directly comparable, owing (in large measure) to differences in the physical condition of the materials employed. As far as possible, standard and reproducible methods of preparation have here been adopted.

The results obtained have been tentatively ascribed to the formation of unstable intermediate compounds between the two oxides present. The increased rates of decomposition may be referred to adsorption effects, but the large temperature changes point strongly to the actual participation of the added oxides in the reaction. Direct evidence was given in certain mixtures of the production of relatively stable complexes.

A later article will continue the study of systems of the types here examined, with particular reference to the Brin oxygen process and the important question of "promoters."

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

## THE PREPARATION AND STUDY OF THE RARER ALKALI BROMATES. RUBIDIUM BROMATE.

BY HAROLD D. BUELL AND C. R. McCROSKY.

Received June 8, 1921.

Some time ago the preparation and some of the properties of cesium bromate were discussed in *THIS JOURNAL*.<sup>1</sup> In the present paper the work has been extended to the rubidium bromate, which like the cesium salt, has had no mention in chemical literature. Some further data on cesium bromate have been added in this paper.

### Preparation of Rubidium Bromate.

A sample of rubidium chloride, of doubtful purity, was converted into the alum<sup>2</sup> and this was recrystallized several times. The solution of the pure alum was digested with an excess of barium carbonate on the hot plate for several hours, and after filtering, treated with barium hydroxide and then with carbon dioxide. After again filtering, the solution gave no tests for traces of aluminum, barium, potassium, cesium or sulfate.

<sup>1</sup> McCrosky and Buell, *THIS JOURNAL*, 42, 1786 (1920).

<sup>2</sup> Browning, "Introduction to the Rarer Elements," John Wiley and Sons Co., 1919, p. 15.

It was now treated with an excess of pure bromic acid and allowed to crystallize. The product was recrystallized three times for analysis.

### Analysis of the Substance.

The finely powdered salt was dried at 115° until it became constant in weight. The results recorded in the following tables are those obtained from analyses carried out in the same manner as those made in the examination of cesium bromate.<sup>1</sup>

TABLE I.

#### IODIMETRIC METHOD OF ANALYSIS.

Wts. of RbBrO <sub>3</sub> taken. G.	RbBrO <sub>3</sub> obtained by analysis. G.	Difference. G.
0.0724	0.0721	-0.0003
0.1129	0.1132	+0.0003
0.1116	0.1111	-0.0005
0.0831	0.0831	0.0000
0.0771	0.0768	-0.0003
0.0591	0.0585	-0.0006
0.0847	0.0839	-0.0008

#### PRECIPITATION METHOD OF ANALYSIS.

##### Reduction with Hydrazine Hydroxide.

0.1079	0.1083	+0.0004
0.0826	0.0829	+0.0003
0.0897	0.0908	+0.0011
0.1182	0.1183	+0.0001

### The Solubilities of Rubidium and Cesium Bromates.

In Tables III and IV appear the values obtained for the solubilities of rubidium and cesium bromates at several temperatures. The method for making the determinations was modeled after that used by Buchanan.<sup>3</sup>

TABLE III.

#### SOLUBILITY OF RUBIDIUM BROMATE IN 100 G. OF WATER.

At 25°. G.	30°. G.	35°. G.	40°. G.	
2.994	3.584	4.310	5.104	
2.895	3.578	4.247	5.116	
2.917	3.509	4.295	5.021	
2.917	3.559	4.269	5.092	
2.93	3.55	4.28	5.08	Average

TABLE IV.

#### SOLUBILITY OF CESIUM BROMATE IN 100 G. OF WATER.

At 25°. G.	30°. G.	35°. G.	
3.627	4.484	5.357	
3.664	4.573	5.410	
3.710	4.525	5.215	
3.66	4.53	5.32	Average

<sup>3</sup> Buchanan, *J. Ind. Eng. Chem.*, 12, 448 (1920).



### Melting Points.

The melting points of cesium and rubidium bromates were determined by the use of a platinum-platinum-rhodium thermocouple, inserted in a bath of fused anhydrous zinc chloride.<sup>4</sup> The salts were placed in capillaries in the bath near the couple. The thermocouple was calibrated by comparing with the accepted melting points of pure potassium dichromate (396°), silver bromide (427°) and thallous chloride (429°). The melting point of cesium bromate was found to be approximately 420°, and that of rubidium bromate 430°. Potassium bromate, even after careful purification, was found to melt at 405°, well below the accepted value of 434°. The same value was obtained when the latter salt was sealed in the capillary. The values, above, are the averages, in each case, of 8 or 10 readings, all of which checked closely.

### Crystalline Structure.

The authors are indebted to Dr. Charles H. Richardson, head of the Department of Mineralogy of Syracuse University for the following data on the crystalline structure of the two bromates.

The crystals from the water solution of both bromates were small and cube-like, but the polarizing microscope showed that they were not isometric (or isotropic) but anisotropic. Both bromates gave perfect uni-axial interference figures, showing definitely that they crystallize in either the tetragonal or the hexagonal system. Under the microscope the hexagonal system may yield crystals, cube-like in aspect, but this is not true in the tetragonal system. In a few instances the outlines of the crystals showed, with reasonable certainty, that they belonged to the hexagonal system. Unsuccessful attempts were made to secure crystals large enough to measure the interfacial angles on a reflecting goniometer. From the work done, however, it would seem that both the cesium and rubidium bromates belong to the hexagonal system. Examination showed that they were optically positive.

For determining the index of refraction of the two bromates a definite series of immersion fluids, commonly used as standards, was used. When compared with methylene iodide, with an index of refraction of 1.74; carbon disulfide, 1.768; sulfur dissolved in methylene iodide, 1.83; molten sulfur, 1.93;  $\alpha$ -sulfur, 1.95; and  $\beta$ -sulfur, 2.038; it was found that the bromates had a still higher index of refraction. The index of refraction of yellow phosphorus (2.144) was a little below, while the value for mercuric iodide crystals from an aniline-quinoline solution (2.22) was a little above that of the bromates. It appears therefore, that the index of refraction of the bromates falls between 2.144 and 2.22. Further work is necessary for the absolute determination of these indices.

### Summary.

Rubidium bromate is prepared by a method similar to the one used in the preparation of cesium bromate.

<sup>4</sup> THIS JOURNAL, 40, 1662 (1918).

Some comparative solubilities of cesium and rubidium bromates are given.

The approximate melting points and data on the crystalline structure of the bromates are included in this work.

SYRACUSE, NEW YORK.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]  
**MANGANESE IN THE CATALYTIC OXIDATION OF AMMONIA.**

BY CHARLES SNOWDEN PIGGOT.

Received June 9, 1921.

The purpose of the investigation<sup>1</sup> was to study the use of manganese as a constituent of catalysts for the oxidation of ammonia. Inasmuch as a considerable amount of work had been done on the use of manganese dioxide mixed with other metallic oxides as a catalyst for the oxidation of carbon monoxide,<sup>2</sup> it was decided to investigate these and similar mixtures for the catalytic oxidation of ammonia.

However, it was anticipated that these finely divided active catalysts would, like finely divided platinum, prove to be too active for this purpose and consequently show a low efficiency. It was thought that this could be overcome if these materials were combined as alloys and superficially oxidized.

The investigation is, therefore, divided into two parts: first, the study of the oxide catalysts; and second, the study of manganese alloys.

### Oxide Catalysts.

**Manganese Dioxide.**—Ordinary manganese dioxide was found to have little catalytic effect on the oxidation of ammonia, but when in a state of fine sub-division it acted as a catalyst for this reaction.

It was prepared by adding powdered potassium permanganate to cold conc. sulfuric acid and allowing the permanganic acid thus formed to decompose spontaneously into manganese dioxide and oxygen.<sup>3</sup> It was then washed by decantation until free from sulfates, filtered and partially dried on a water-bath. When the water content had been reduced to about 50% it was subjected to a pressure of 2818 kg. per sq. cm. for 24 hours. The resulting cake was broken up and completely dried in a stream of oxygen at 130–140°. When tested<sup>4</sup> on ammonia this material showed considerable catalytic effect, as is shown in Table I following.

<sup>1</sup> This investigation was carried on throughout part of 1919 and 1920.

<sup>2</sup> Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, 12, 213–21 (1920); Rogers, Piggot, Bahlke and Jennings, *THIS JOURNAL*, 43, 1973 (1921).

<sup>3</sup> Fremy, *Compt. rend.*, 82, 1231 (1876).

<sup>4</sup> The difficulties associated with the quantitative estimation of oxidized nitrogen as described later in this article applied equally here.

TABLE I.—MANGANESE DIOXIDE.

Temp. of catalyst = 800°. NH<sub>3</sub>, 300 cc./min.

Time of contact = 0.05 sec. Air, 3200 cc./min.

Time of run 50 minutes. 1.0 cm. layer.

In.	HNO <sub>3</sub> g. Out.	Eff. %.	Remarks.
37.74	23.88	63.27	not pressed
37.86	24.19	63.90	not pressed
37.74	23.72	62.85	not pressed
38.23	36.52	95.44	pressed
38.63	30.64	79.31	pressed
38.85	29.46	75.84	pressed

Though functioning catalytically the oxide undergoes some change during the reaction. The color changes from black to a light yellowish-brown, the material having changed apparently from the dioxide to a lower oxide of manganese.

**Mixture of Oxides.**—Precipitated manganese dioxide when mixed with various proportions of silver oxide or copper oxide or with both of these oxides produces a catalyst which is quite active in the oxidation of ammonia.

The manganese dioxide used for these mixtures was prepared by treating a concentrated solution of potassium permanganate at 80° with methyl alcohol, filtering on a Büchner funnel, washing and drying to about 50% water content, this latter being determined by analysis. A weighed quantity of this paste was made into a fine suspension in water and the proper amount of silver added in the form of silver nitrate solution. Silver oxide was then precipitated on the manganese dioxide by means of a slight excess of strong sodium hydroxide solution. The two oxides quickly settle out as a single precipitate. When silver and copper were used together they were added in the form of their nitrate solutions as above. When copper alone was added it was usually added as the sulfate and precipitated by sodium carbonate. In any case the precipitates were washed by decantation until free from alkali or sulfates, filtered with suction and dried in a current of oxygen at 130–140°. The dry cake was broken up, screened to convenient size and used for testing.

Catalysts so made have proved to have considerable activity, are very porous, thus offering a very large surface, and are quite resistant to the high temperatures of the reaction, *i. e.*, they show no tendency to sinter together even when the temperature is raised to 1000° or more. The activity can be more or less closely controlled by the method of preparing the catalytic mixture; mixtures containing the constituents in a very fine state of subdivision and in intimate contact being much more active than those in which the reverse is true.

The disadvantages of such catalysts are softness, tendency to crumble and produce fines which clog the gas passages, their tendency to take

up moisture due to their extreme porosity, the fact that in contact with a liquid they disintegrate, and that liquid nitric acid will dissolve out the silver or copper oxides. Tables II, III and IV show the results of the tests on these oxide mixtures.

Manganese dioxide when prepared by the Fremy method and mixed with silver oxide, copper oxide, or mixtures of both, produces materials which are such vigorous oxidizing catalysts that the ammonia is largely converted into nitrogen and water, with a consequent low efficiency for nitric acid.

TABLE II.—MIXTURES OF OXIDES.

Composition:  $\text{MnO}_2$  (Fremy), 71.43%;  $\text{CuO}$ , 21.43%;  $\text{Ag}_2\text{O}$ , 7.14%; dried at  $135^\circ$ . Time of contact, 0.11 sec.  $\text{NH}_3$ , 300 cc./min. Air, 3200 cc./min. Temp. of cat.,  $800^\circ$ . Time of run, 50 min. 1.8 cm. layer.

In.	$\text{HNO}_3$ g. Out.	Efficiency %
38.63	18.85	48.77
38.77	21.10	54.41

Manganese dioxide prepared by treating hot ( $100^\circ$  approx.) potassium permanganate solution with methyl alcohol is relatively coarse in structure and consequently not so active. This type was used in preparing mixtures of which the following is a fair example. Though not so active an oxidizing catalyst it gave greater efficiencies based on the nitric acid yield.

TABLE III.—MIXTURES OF OXIDES CONTAINING COARSER MANGANESE DIOXIDE.

Composition:  $\text{MnO}_2$ , 60%;  $\text{CuO}$ , 40%; dried at  $140^\circ$ . 4 cm. layer. Time of contact, 0.2 sec.  $\text{NH}_3$ , 300 cc./min. Air, 3500 cc./min. Temp. of cat.,  $800^\circ$ . Copper precipitated as carbonate.

In.	$\text{HNO}_3$ g. Out.	Eff. %
38.10	33.80	88.96
38.60	37.74	97.71
38.62	33.79	87.50
38.62	38.29	96.57
38.23	36.69	95.98

Manganese dioxide was prepared as for the  $\text{MnO}_2$ - $\text{CuO}$  mixture described above and mixed with silver oxide, the latter being precipitated on the former from the nitrate solution by sodium hydroxide. The efficiency, not high at first, rapidly decreased. The time of exposure of each charge was 6 hours.

TABLE IV.—OXIDES OF MANGANESE AND SILVER.

Composition:  $\text{MnO}_2$ , 62.5%;  $\text{Ag}_2\text{O}$ , 37.50%. 1 cm. layer.

Time of contact. Sec.	NH <sub>3</sub> cc./min.	Air cc./min.	In.	HNO <sub>3</sub> G.	Out.	Temp. cat. °C.	Eff. %.
0.082	400	4200	50.67	29.37	650	57.9	
0.082	400	4200	50.67	29.86	650	58.8	
0.082	400	4200	51.36	37.42	790	72.86	

TABLE IV (continued).

Time of contact. Sec.	NH <sub>3</sub> cc./min.	Air cc./min.	NHO <sub>2</sub>		Temp. cat. ° C.	Eff. %.	
			In.	Out.			
0.082	400	4200	51.50	34.65	820	67.20	
0.057	300	3000	38.52	24.69	800	64.11	NH <sub>3</sub> passing
New Charge 2 cm. layer.							
0.13	200	2600	25.49	21.55	700	84.52	
0.13	200	2600	25.42	20.04	700	81.04	
0.13	200	2600	25.42	20.60	800	79.00	
0.13	200	2600	25.42	19.34	800	76.09	NH <sub>3</sub> passing
0.057	300	3100	38.23	22.62	800	57.16	"

## II. Manganese Alloys.

The variable valence of manganese together with its other chemical properties, recommended it as a good catalytic agent if brought into intimate contact with suitable promoters. It was thought that this intimate contact might well be obtained in an alloy. The advantages of an easily workable metallic catalyst are many; as for instance the possibility of making connections and reaction chambers of it and the weaving of gauzes for the actual contact material.

S. F. Zhemchuzhnii and V. K. Petrashevich<sup>5</sup> state that they have been able to cold draw a manganese alloy of the composition 1.1% Fe, 3.53%-Cu, 0.50% Al, 0.12% Si and 94.75% Mn, to a wire 1 to 1.5mm. diameter without annealing between passes. None of the alloys used in this investigation, though more or less ductile, exhibited such ductility as indicated by the above.

Some 6 months of the investigation were devoted to the problem of obtaining a manganese alloy relatively free from impurities (Fe, C, Si). This proved very difficult, and has not been entirely solved up to the present time.

Crucibles of carbon, silicon, or porcelain were of course out of the question, and the usual magnesite crucibles proved to be too porous and frail for melting satisfactorily 200- to 400-g. charges of material.

Alundum crucibles tended to adsorb large quantities of the molten manganese, forming a slag coating which was extremely hard. This difficulty was only partially overcome by lining the crucibles with magnesium oxychloride. The most satisfactory crucibles so far tried were made from a magnesite-iron oxide mixture of about the same composition as that used in making the ordinary magnesite brick for iron smelting purposes.

When using a molybdenum-wound "hydrogen" furnace, the hydrogen formed many "blow holes" in the ingots, the small magnesite crucibles being too frail to permit pouring.

With an electric-resistance vacuum furnace the volatilization of the manganese

<sup>5</sup> Zhemchuzhnii and Petrashevich, *Bull. acad. sci.*, 1917, 863-76.

was excessive even when the furnace was filled with hydrogen under slightly reduced pressure.

The best results have been obtained by using the magnesium oxide—iron oxide crucible as stated above, and a Seger gas furnace. The melt was covered with fused sodium borate as a flux, and the charge was protected as much as possible from contact with the furnace gases by enclosing the crucible in a fire-clay muffle. The best obtainable thermit-process manganese, and electrolytic copper and silver were used. A comparatively large charge was melted and the best of the metal poured into a steel mould coated with graphite, giving a rod 12 mm. in diameter by 15cm. long, which required about half the metal of the melt. This rod was then turned on a lathe and the turnings after oxidizing were used as catalysts.

Considerable time was devoted to various methods of oxidizing metallic surfaces so as to give a firm and adherent coating as well as one of maximum activity. Various gauzes, especially those containing manganese were investigated with this end in view, the final result being the method of electrolytic oxidation described below.

The preliminary oxidation of the catalysts was done electrolytically, the turnings being placed in a porous cup and made the anode by thrusting a platinum wire into the mass. The electrolyte used was 0.1 *N* sodium hydroxide solution. A current of 0.5 to 1.0 ampere was passed for from 3 to 4 hours, the potential across the electrodes being 10.0 to 15.0 volts.

This treatment caused the material to be thoroughly oxidized superficially, with a very adherent dark brown coating. After being washed and dried it was ready for testing.

It was found in the course of the investigation that it was not essential to oxidize the alloys before using, for like the platinum gauzes they could be "activated" by exposure at 600–700° to the ammonia-air mixture, for several hours. However, the electrolytic method was more rapid and satisfactory, and was the usual method employed.

#### Analytical Difficulties.

A very troublesome problem was the devising of a suitable testing and analytical method, and the building of a satisfactory apparatus to put the same into operation. The chief difficulty was to prevent as much as possible the decomposition of the nitric oxide once formed and to bring about its *complete* oxidation to nitrogen dioxide or the higher oxides and to insure their absorption. This was accomplished by using oxidation towers of large volume, water vapor in the form of saturated steam, and vigorous agitation by means of high-speed stirring.

Nitrogen oxides are very difficult to absorb, as is also ammonium nitrate, the latter especially so when in the condition of a colloidal "smoke." Efforts were first directed toward absorbing the oxides of nitrogen in towers of various types. Soda-lime, sodium hydroxide, water, hydrogen peroxide, potassium permanganate solution, conc. sulfuric acid, etc., were tried separately and in conjunction.

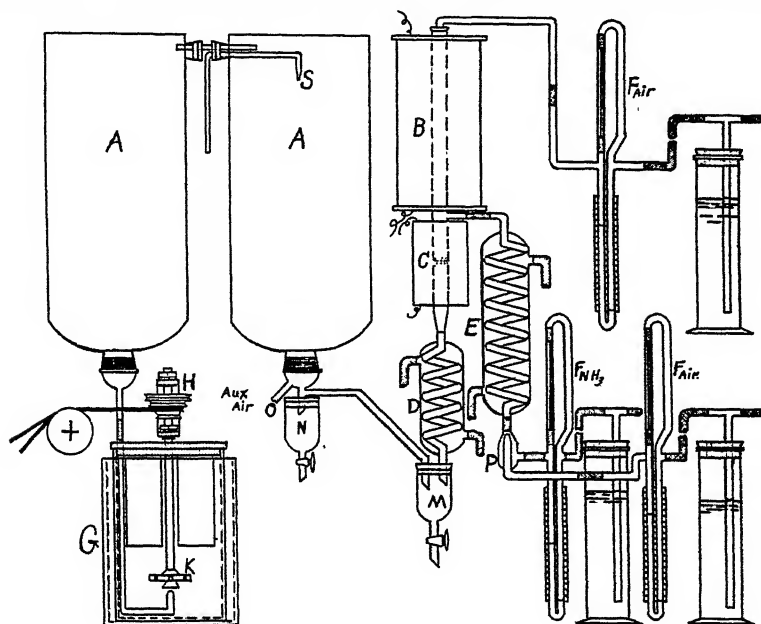
The efficiency was to be calculated on the basis of the oxygen used up. This involved accurate measurement of flows of affluent and effluent gases and absolute oxidation and absorption of the nitrogen oxides. All such methods proved unavailing. Various types of flow-meters were made and tried but none could be devised which

would measure accurately the varying concentrations of the various oxides of nitrogen which passed through it, without being affected thereby.

Conc. sulfuric acid may absorb oxides of nitrogen quantitatively, as stated by Nernst, in small quantities and on long exposure; but it was found entirely inadequate under the conditions of this investigation.

### Apparatus.

The apparatus used in the investigation is shown diagrammatically in the accompanying drawing. *A, A* are two 10-liter aspirating bottles which serve to give volume, and allow time for the oxidation of nitric oxide to nitrogen dioxide or the higher oxides. A jet of low-pressure steam is passed in at *S* which furnishes water for the formation of nitric acid which is drawn off at *N*. *B* is a Hoskins electric furnace and *C* the catalyst, supported on a Witt plate, the whole being surrounded by an auxiliary heating unit which serves to start the reaction and to maintain it at the proper temperature. The clay combustion tube which contains the catalyst passes through



the two heating units and is provided in one side with a porcelain tube through which the mixed gases enter. It is connected below with a water-cooled condenser *D* which serves to cool the products of the reaction quickly. The catalyst bed is provided with a small quartz bulb in which is a thermocouple whose wires lead to a Leeds and Northrup compensating potentiometer. *E* is a coil condenser, which serves as a preheater of the mixed gases, through the jacket of which steam is passed at from 140 to 210 g. per sq. cm. pressure. *P* is a mixing chamber for the ammonia and air, while  $F_{NH_3}$ ,  $F_{Air}$  are flow-meters for the measurement of these gases respectively. *G* is the absorption apparatus consisting of two battery jars with cold water circulating in the annular space between. The inner jar contains sodium hydroxide solution which is kept stirred by the stirring mechanism *H* which revolves at a speed of 10,000–20,000 r. p. m., the stirring head *K* being heavily gold plated. This stirring head is so con-

structed that the entering gases and vapors are sucked up at the center and thrown out through the radial holes, which at the speed of operation brings about an emulsoid condition which insures a very thorough mixing and accomplishes complete absorption of the vapors of nitric acid and the oxides of nitrogen. Baffle plates are provided to prevent a circular motion of the liquid and to prevent the latter from being thrown out of the container. It was found necessary to cool the solution, as otherwise the heat produced by the rapid stirring during a run was sufficient to bring the solution almost to its boiling temperature. The water (usually slightly acid) produced by the oxidation of the ammonia is collected and drawn off at *M*. If desired, an auxiliary stream of air could be passed in at *O*, but this was seldom used.

The flow-meters were carefully calibrated at average room temperature, 25°, and were used only on the gas with which they had been previously calibrated.

### Methods of Testing.

In making a run the following procedure was usually adopted. 1000 cc. of *N* sodium hydroxide solution was placed in the adsorption apparatus *G*; and the catalyst, placed at *C*, heated externally to about 600°. The furnace *B* was heated to its maximum temperature (950–1000°) and steam passed in at *S* and through *E*. Ammonia from a steel cylinder, and air, measured by their respective flow-meters, were passed into the mixing chamber *P*. The quantity of air mixed with the ammonia at this point was usually only sufficient to furnish a volume of oxygen equal to that of the ammonia; the remaining air for the completion of the reaction being passed through the other air flow-meter and down through the hot furnace *B*, meeting the ammonia-air mixture just before contact with the catalyst. This air was heated by the furnace *B* to about 300° to 400°, while the mixture passing through the preheater *E* was heated not above 90–100°, thus ensuring no decomposition of the ammonia. The liquids which collect at *M* and *N* were drawn off from time to time and added to the sodium hydroxide solution at the end of the run. At first runs of 100 minutes were made, but later 50-minute runs were used and this time was maintained throughout the remainder of the investigation.

The gases issuing from the second reaction chamber were by-passed and allowed to escape for some time until the run became stabilized and everything was working properly before a test was begun.

The ammonia entering the apparatus was calculated as g. of nitric acid,  $\text{HNO}_3$ , due correction being made for temperature at the flow-meter. At the end of the run the solution in *G* was measured and its normality determined by titrating a 10.00cc. sample with *N* hydrochloric acid using phenolphthalein as indicator. From this the g. of nitric acid produced was obtained and the percentage efficiency calculated.

To the 10.00cc. sample of solution from *G*, taken above, when just neutralized, was added an additional 10.00 cc. of *N* sodium hydroxide solution, any ammonia thus liberated was boiled off and the solution back titrated with *N* hydrochloric acid. In this way the quantity of ammonia



which passed the catalyst unoxidized was determined and could be corrected for. This procedure however was not always necessary as even a slight trace of ammonia passing the catalyst would fill the reaction chambers with a dense white cloud of ammonium nitrate and thus indicate its presence.

A number of preliminary test runs were made to determine the effect of glass, quartz, porcelain, and other materials on the decomposition of ammonia and the oxides of nitrogen when formed. All those materials were found to favor the decomposition to a greater or less extent, quartz being the most active catalyst for this decomposition.

A clay combustion tube was found to give the least decomposition. Condensed results of this investigation are shown briefly in the following tabulation. The same catalyst was used throughout.

Rate of NH <sub>3</sub> , 80 cc./min.		Eff. %
Temp. of cat. C.	Material.	
900	Quartz	33.40
830		34.10
800		40.48
650		39.91
630	Pyrex	35.50
700		44.10
800		59.10
845	Clay	70.70
850		75.60
900		73.60

After the clay tube was adopted an idea of the effect of heat and time of heating, on the decomposition of ammonia, was obtained by locating the catalyst bed at various points up and down in the electric furnace.

Rate of NH <sub>3</sub> , 80 cc./min.		
Temp. of cat. C.	Eff. %	Position of catalyst bed.
830	51.91	5 cm. from lower end
835	57.52	7.5 cm.
845	70.70	Center of furnace
850	68.62	
900	77.50	5 cm. from upper end
750	74.10	
850	81.12	

These results led to the adoption of the arrangement shown in the drawing of the apparatus, whereby all the ammonia and about  $\frac{1}{2}$  of the air, after being warmed to about 80° enter the reaction tube just above the catalyst bed and are quickly swept down over the latter by the remaining air which, having passed through the furnace, was heated to about 300°.

When a very reactive catalyst was being tested no heat at all was necessary in the larger furnace; in fact it was sometimes necessary to take precautions to prevent the catalyst from melting.

## Experimental.

As has been indicated, a number of manganese alloys were made. The results of the tests of those which were examined are shown in the tables below.

TABLE V.  
ALLOY NO. 1.

Composition: Mn, 48.78%; Cu, 37.25%; Ag, 12.70%; Fe, 0.85%; SiO<sub>2</sub>, 0.50%.  
Run, 50 min. 0.5 cm. layer. Temp. of cat., 800°.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Air. Cc./min.	In.	HNO <sub>3</sub> . G.	Out.	Eff. %.
0.043	200	2000	25.58		15.88	62.08
0.043	200	2000	25.58		16.06	62.60
0.028	300	3000	38.52		23.18	60.20
0.028	300	3000	38.63		24.00	62.10
0.028	300	3000	38.63		24.82	64.25
0.022	400	4000	50.98		31.63	62.04
0.022	400	4000	51.36		32.50	63.20

An alloy containing a somewhat higher percentage of manganese with consequent lower percentages of copper and silver gave better yields of nitric acid. The impurities of iron and silicon were also higher. Results of test of this alloy (No. 2) are shown in Table VI.

TABLE VI.  
ALLOY NO. 2.

Composition: Mn, 59.60%; Cu, 27.40%; Ag, 8.55%; Fe, 3.25%; SiO<sub>2</sub>, 1.25%.  
Run, 50 min. 0.5 cm. layer.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Air. Cc./min.	In.	NHO <sub>3</sub> . G.	Out.	Temp. of cat. ° C.	Eff. %.
0.107	80	800	10.48		8.09	838	77.25
0.107	80	800	10.48		8.38	842	79.95
0.107	80	800	10.13		7.66	848	75.60
0.045	100	2100	12.92		9.64	800	74.70
0.045	100	2100	12.84		11.71	800	91.05
0.045	100	2100	12.79		7.12	800	56.00
0.045	100	2100	12.84		8.32	800	64.70
0.051	160	1600	20.88		18.12	856	86.80
0.043	200	2000	25.68		20.66	800	80.40
0.043	200	2000	26.01		23.31	855	89.60
0.043	200	2000	26.01		23.97	857	92.10
0.022	400	4000	52.03		43.72	800	84.03
0.022	400	4000	51.88		39.62	800	76.50
0.022	400	4000	52.02		44.20	800	85.13
0.022	400	4000	51.88		40.20	800	77.68
0.022	400	4000	51.50		40.88	800	79.30
0.022	450	4000	51.40		39.50	800	76.80
0.019	400	4600	58.15		44.10	800	75.80
0.019	450	4600	57.90		44.10	800	76.16
0.019	450	4600	57.76		43.66	800	75.60
0.017	500	5000	64.37		46.00	800	71.00
0.017	500	5000	61.60		46.43	800	71.90

An alloy high in manganese was made and tested to determine the limiting proportion of manganese. This alloy was not analyzed but it is believed that its composition closely approximates the proportions of the constituents which were weighed into the melt: *i. e.*, Mn, 80%; Cu, 10%; Ag, 10%.

TABLE VII.

## ALLOY No. 3.

Composition: Mn, 80%; Cu, 10%; Ag, 10%. Run, 50 min. 0.5 cm. layer. Temp. of cat., 800°.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Air. Cc./min.	HNO <sub>3</sub> .		Eff. %.
			In.	Out.	
0.032	200	2800	25.58	13.48	52.85
0.032	200	2800	25.49	13.45	52.80
0.027	300	3200	38.23	22.80	59.65
0.022	400	4800	50.80	23.56	46.38

It is evident from the above that the maximum manganese content lies well below 80%.

Alloy No. 4 of the following composition: Mn, 54.79%; Cu, 43.77%; Fe, 1.22%; Si, 0.09%, containing no silver at all, showed less than 25% efficiency.

Alloy No. 5 was made with the idea of duplicating No. 2. Analysis showed that it contained Mn, 56.07%; Cu, 32.81%; Ag, 9.96%; Fe, 1.23%; Si, 0.07%.

TABLE VIII.

## ALLOY No. 5.

Run, 50 min. 0.5 cm. layer.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Air. Cc./min.	HNO <sub>3</sub> .		Temp. of cat. °C.	Eff. %.
			In.	Out.		
0.036	200	2400	25.58	14.91	700	58.27
0.027	300	3200	38.37	20.34	700	53.06
0.027	300	3200	38.62	18.67	700	48.34
0.027	300	3200	38.52	19.79	800	51.38
0.027	300	3200	38.37	18.27	800	47.60
0.027	300	3200	38.52	20.10	800	52.18
0.027	300	3200	38.52	20.85	850	54.13

## Discussion.

As stated in the literature, manganese dioxide was found to have some effect as a catalyst for the oxidation of ammonia.

Early in this investigation it was shown that this effect can be greatly increased by the method of preparing the oxide. The physical structure of the material is of great importance, extremely fine subdivision giving a large adsorbing surface with very small pores being conducive to greater activity.

It was also shown that suitable promoters have a great influence on the catalytic activity of the material. Manganese dioxide is apparently

reduced, in the course of the reaction, to some lower oxide of manganese, and the promoter serves to aid the oxygen to reoxidize it back to the dioxide. This is indicated by the fact that when used alone, after several hours, the greater part of the manganese dioxide is reduced to the lower reddish colored oxide. That part of the material which remains black ( $\text{MnO}_2$ ) is always a thin layer on the top of the catalyst bed, being that portion which first comes into contact with the air and is consequently more readily re-oxidized. When a promoter is mixed with the manganese dioxide very little of the material shows reduction after several hours' use; in this case the reduced area (if any) is always at the bottom of the catalyst bed and is never very great.

Manganese dioxide produced by the action of methyl alcohol on potassium permanganate and, consequently consisting of comparatively coarse particles, was always less completely re-oxidized by the promoter than that prepared by the Fremy method, thus indicating qualitatively the relation of subdivision to reactivity.

When silver and copper were used together as promoters with manganese dioxide prepared by the Fremy method (Table II) there was no indication whatever of permanent reduction of the latter. This would indicate that these two materials tend to act as very efficient carriers of oxygen to the manganese.

On the other hand, however, the temperature and oxygen pressure at which the material was used was far above the dissociation temperature of silver oxide, which would lead to the conclusion that finely divided silver alone is as effective a promoter as silver oxide. This agrees with the conclusion of Lanning<sup>6</sup> drawn from his work on the carbon monoxide catalyst, in this laboratory.

The low yields of nitric acid obtained from the 3-component mixtures as shown in Table II coupled with the fact that no ammonia was detectable in the effluent gases indicates that this material (the catalyst used for carbon monoxide oxidation) is very active and that a very small time of contact is sufficient for it also to favor the decomposition of the nitric oxide once formed. This is analogous to the behavior of platinum black when used alone for this reaction. Some mixture should be possible which would be just active enough to favor the formation of nitric oxide while preventing the liberation of elementary nitrogen. Such a mixture seems to be approximated by that shown in Table III.

It was shown that alloys of manganese exist which possess considerable catalytic activity for this reaction and the data point toward an alloy of rather restricted composition which gives promise of high efficiency. Such an alloy should exist within the following limits of composition: Mn, 55-65%; Cu, 25-35%; Ag, 5-15%; Fe, 1-5%; Si, 0-3%.

<sup>6</sup> Lanning, *Dissertation, Johns Hopkins Univ.*, June, 1920.

Small changes of composition apparently have great influence on the catalytic activity and efficiency and it is believed that further investigations in this more restricted field will develop a catalyst which will yield an efficiency of 90 or 95%, or even greater.

### Summary.

Due to mechanical difficulties encountered during this investigation the above experimental data are not as extensive or complete as would be desired. It is believed, however, that the way has been cleared for a more comprehensive and exhaustive study of this subject and that in the future, such can be carried out without great difficulty.

Mixtures of especially prepared manganese dioxide containing promoters of copper and silver oxides have been made which possess great catalytic activity for the oxidation of ammonia by air.

Attention is called to the mixture of manganese dioxide and cupric oxide shown in Table III. This mixture apparently possesses as great efficiency as platinum and during the tests showed no appreciable deterioration after 6 hours continuous run.

A method is indicated for the preparation of manganese alloys relatively free from impurities. Alloys of manganese with silver and copper have been made which serve as catalysts for the oxidation of ammonia, and the approximate composition of an alloy is indicated which should give a high efficiency for this reaction.

Thanks are here expressed to Professor J. C. W. Frazer for advice and suggestions during the course of this investigation.

BALTIMORE, MARYLAND.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY. No. 8.]

## THE CRYSTAL STRUCTURES OF SODIUM CHLORATE AND SODIUM BROMATE.

BY ROSCOE G. DICKINSON AND ELBRIDGE A. GOODHUE.

Received June 9, 1921.

### 1. Introduction.

Before the present research was undertaken, some X-ray work had already been done on sodium chlorate and bromate. It is mentioned in Bragg's "X-rays and Crystal Structure"<sup>1</sup> that the sodium and chlorine atoms in the chlorate are located approximately as in sodium chloride, but no data are given. Jaeger<sup>2</sup> published Laue photographs showing that the symmetry of the atomic arrangement of the chlorate is at most

<sup>1</sup> Bragg, "X-Rays and Crystal Structure," G. Belland Sons, Ltd., London, 2nd Ed., p. 173.

<sup>2</sup> Jaeger, *Verslag akad. Wetenschappen Amsterdam*, **17**, 1 (1915).

no greater than that of pyrite, but he did not attempt to deduce the structure from his results.

Since the completion of the present research in which the X-ray spectrometer was employed, a paper has appeared by Kolkmeijer, Bijvoet, and Karssen,<sup>3</sup> who studied the structures of these substances by means of powder photographs. Although their experimental method was different from ours, they arrived at the same type of structure that we had chosen; but the location of the atoms in their structure is not in full agreement with our conclusions. A comparison of their results with ours is given in a later section of this article.

This research was carried on with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our indebtedness.

## 2. Apparatus and Procedure.

The crystals used were prepared either by slow cooling of a saturated aqueous solution in a thermostat, their formation taking place between 40° and 30°, or by the slow evaporation of a solution at room temperature. With the aid of a suitable device the desired faces were ground on the crystals using fine emery on plate glass with carbon tetrachloride as a lubricant. The accuracy of the grinding was better than 15'. Crystal faces thus prepared were set up on a holder which defined vertically the area of crystal presented to the X-ray beam. The crystal face was always chosen sufficiently long horizontally to cover the entire incident beam, even at small angles of reflection. The crystal holder was so constructed that it could be easily removed and accurately replaced on the spectrometer. In order to be able to compare intensities of reflection from various faces, a reference crystal was set up on a second holder interchangeable with the first. The crystals gave sharp reflections and were apparently good specimens.

The source of X-rays was a fine-focus Coolidge tube of the radiator type provided with a molybdenum target set in copper. The filament current was supplied by a 10-volt storage battery; the tube current was measured with a milliammeter and was kept constant with the aid of a variable resistance in the filament circuit. Except for the points mentioned the apparatus was substantially the same as that used previously.<sup>4</sup>

In the measurement of intensities an integration method similar to that described by W. H. Bragg<sup>5</sup> was employed. The ionization chamber was set on a previously measured angle of maximum reflection; then the crystal was uniformly rotated through an angular range sufficient to give sub-

<sup>3</sup> Kolkmeijer, Bijvoet and Karssen, *ibid.*, 23, 644 (1920).

<sup>4</sup> Dickinson, *THIS JOURNAL*, 42, 85 (1920).

<sup>5</sup> W. H. Bragg, *Phil. Mag.*, 27, 881 (1914).

stantially all of the peak in question opportunity to reflect, and the total deflection of the electroscope was read. To correct for the general radiation similar integrations were made through equal angular ranges on each side of the peak, and a mean subtracted from the deflection at the peak. The slit defining the incident beam was kept at 0.3 mm. In determining the chamber angles, the chamber slit was 0.5 mm.; but in measuring the intensities the chamber slit was opened to 1.0 mm. to avoid affecting them by any small errors in the chamber angle. In the last step measurements on the reference crystal were alternated with those on the face in question.

In order to compare intensities of reflection from different faces, it was necessary to prepare all faces by grinding in the same manner. Compton<sup>6</sup> had observed that "if the reflecting surface of a crystal of calcite is roughened by grinding, the reflection coefficient is some three times as great as from a cleavage face." With both sodium chlorate and sodium bromate it was found that with natural faces that had not been cleaved there was a similar effect, and that the increase in intensity on grinding, amounting in some cases to over 100%, was greater the smaller the angle of reflection. By turning the crystal face through 180°, as recommended by W. H. Bragg,<sup>5</sup> the effect was shown not to be due to inaccurate grinding. W. L. Bragg, James, and Bosanquet<sup>7</sup> have recently observed the same phenomenon with sodium chloride, using first a cleavage surface. The occurrence of this effect, which is still under investigation in this laboratory, is the rule rather than the exception and seems to indicate that all naturally grown faces, as well as cleavage faces of crystals, are covered by a thin absorbing, but non-reflecting layer.

Another important precaution was found necessary in the present measurements. It is, perhaps, best shown by means of an example. A large (110) face of sodium chlorate was set up not limited vertically by one of the holders described above; the crystal was set with two cube faces vertical and with the other four making angles of 45° with a horizontal plane. The chamber and crystal angles for two reflections were found; with the aid of these, the angles of reflection in the entire region between chamber angles of 2° and 33° were measured, rotating the crystal half as fast as the chamber. In this manner peaks were found at chamber angles of 9° 10', 13° 40', 18° 0', and 27° 0'. If each of these is divided by two and a correction of 11' subtracted from each of the results, the glancing angles 4° 24', 6° 39', 8° 49', and 13° 19' are obtained. These seemed to be the angles of reflection for the second, third, fourth and sixth orders, respectively, consistent with the fundamental equation  $n \lambda = 2d \sin \theta$ ; for on dividing the sines of these angles by 2, 3, 4, and 6, re-

<sup>6</sup> A. H. Compton, *Phys. Rev.*, 10, 95 (1917).

<sup>7</sup> W. L. Bragg, James, and Bosanquet, *Phil. Mag.*, 41, 316 (1921).

spectively, the numbers 0.0384, 0.0386, 0.0384, 0.0384 are obtained. Yet, if the crystal and slits have moderately large vertical dimensions, reflections from a number of atom planes with different indices, but from the same boundary of the crystal, may enter the ionization chamber; moreover, it can be shown analytically that when the crystal is set with an important zone axis horizontal, as in the above case, these reflections, although coming from planes whose spacings are irrationally related to those of the prepared face, may have crystal and chamber angles very nearly in accord with the sine law and thus appear to come from the prepared face. That this had taken place in the case of the (110) spectra was clearly shown photographically. A photographic plate was set up perpendicularly to the incident beam, and in place of the ionization chamber. The crystal (set up as above) was rotated slowly and uniformly through a region sufficient to include the above lines. The reflections which had been called the 2nd, 4th, and 6th orders appeared as a horizontal row of vertical lines. The reflection which had been called the third order showed as a strong vertical line, which was not, however, in a horizontal row with the others. Another strong line was found directly below and partly overlapping the 2nd order. These last two clearly did not belong to the (110) spectra. Other lines from other faces were also in evidence. If this interpretation is correct, it should follow that when the crystal is moved in such a way that (110) remains vertical but the other faces are rotated, and a photograph taken as before, the real reflections from (110) should persist, but those from other faces undergo alteration. A photograph was made in the same manner as the previous one, but with two cube faces horizontal and four vertical. The lines previously called the 2nd, 4th, and 6th orders were the only ones common to the two photographs. By limiting the crystal face vertically to about 5 mm. by means of the holder, and by setting the crystal with no important zone axis horizontal, it was found possible to isolate these three lines for intensity measurement. Similar precautions were taken in the measurements on other faces. It seems likely that failure to observe this precaution is responsible for confusion that has arisen in the literature and that it accounts for cases where one investigator has reported reflections which the other did not find.

### 3. The Experimental Data.

An extended series of observations on sodium chlorate and a few on sodium bromate are given in Tables I and II. Since faces of the form (hok) are geometrically indistinguishable from those of the form (ohk) until the directions of the axes have been chosen, the faces (201), (10 $\bar{2}$ ), (301) and (10 $\bar{3}$ ) were all cut from the same crystal. The same is true of the two faces (111) and ( $\bar{1}\bar{1}\bar{1}$ ). The tabulated values are, in many cases, means of several determinations.



TABLE I.  
REFLECTION DATA FOR SODIUM CHLORATE.

Plane.	Order. n.	Observed angle of reflection (corrected).	Intensity. <sup>a</sup>	Calculated angle of reflection.
(100)	2	6° 12'	1.00	6° 13'
	4	12 28	0.042	12 30
	6	18 53	0.116	18 57
	8	25 33	0.033	25 39
(110)	1	4 23	0.218	4 23
	2	8 47	0.047	8 48
	3	13 14	0.052	13 16
(111)	1	5 22	0.441	5 23
	2	10 47	0.071	10 48
	3	16 18	0.165	16 20
(111)	1	5 21	0.466	5 23
	2	10 45	0.080	10 48
	3	16 16	0.196	16 20
(201)	1	6 56	0.957	6 57
	2	.....	0.00	14 0
(102)	1	.....	0.00	6 57
	2	13 56	0.097	14 0
(301)	1	9 44	0.074	9 51
	2	19 58	0.017	20 1
(103)	1	9 47	0.088	9 51
	2	19 53	0.088	20 1

<sup>a</sup> Intensities are referred to that of second order of (100) of NaClO<sub>3</sub> taken as unity.

TABLE II.  
REFLECTION DATA FOR SODIUM BROMATE.

Plane.	Order. n.	Observed angle of reflection (corrected).	Intensity. <sup>a</sup>	Calculated angle of reflection.
(100)	2	6° 5'	0.284	6° 4'
	4	12 14	0.081	12 13
	6	18 32	0.081	18 31
(111)	1	5 16	0.281	5 16
	2	10 33	0.133	10 33
	3	15 58	0.133	15 57

<sup>a</sup> Intensities are referred to that of second order of (100) of NaClO<sub>3</sub> taken as unity.

#### 4. Derivation of the Crystal Structures.

The type of atomic arrangement in these substances is probably most conveniently arrived at by a method which has been described by Wyckoff,<sup>8</sup> to whom we are also much indebted for personal explanations of the application of the theory of space groups. It is always possible to regard a cubic crystal as built up by the repetition of a unit of structure on a simple cubic lattice; and we can determine the number *m* of molecules (of NaClO<sub>3</sub> or NaBrO<sub>3</sub>) in the unit of structure by means of the equation

<sup>8</sup> Wyckoff, *Am. J. Sci.*, 1, 127, 138 (1920).

$\frac{n^3}{m} = \left( \frac{2 \sin \theta}{\lambda} \right)^3 \frac{M}{N\rho}$ . In this equation  $n$  denotes the order of reflection (based on the simple cubic lattice);  $\lambda$ , the wave length<sup>9</sup> of the X-rays used ( $0.710 \times 10^{-8}$ );  $\theta$ , the angle of reflection from a cube face;  $\rho$ , the density of the crystal;  $M$  the formula-weight of sodium chlorate (or bromate), and  $N$  Avogadro's number ( $6.06 \times 10^{23}$ ). The density has been taken as 2.49 for the chlorate and 3.30 for the bromate.<sup>10</sup> Taking for  $\theta$  the smallest angle at which reflection was found from the cube face with each substance, and substituting the proper values of the other quantities, we get  $n^3/m$  equal to 1.99 for the chlorate and 2.00 for the bromate. If  $n = 2$  and  $m = 4$ ,  $n^3/m$  is 2; and these are the only possible values of  $n$  and  $m$  that bring  $n^3/m$  into close agreement with the values calculated above. For, if the structure be assumed to contain only one kind of sodium atom and one kind of chlorine (or bromine) atom, and not more than three kinds of oxygen atoms, the value of  $m$  can only be 48 or a submultiple of 48; for there are 12 equivalent directions in the cubic tetartohedral point-group, and there may be 1, 2, or 4 lattice points associated with the unit of structure. This shows that the crystal structure may be obtained by the repetition of a unit containing 4  $\text{NaClO}_3$  (or 4  $\text{NaBrO}_3$ ) on a simple cubic lattice.

The dimensions of the lattices can probably be most accurately obtained from the densities. Thus, the length  $d_{100}$  of the side of the unit cube may be calculated by the equation,

$$d_{100} = \left( \frac{4M}{N\rho} \right)^{1/3}$$

This gives for sodium chlorate  $6.56 \times 10^{-8}$  cm., and for sodium bromate  $6.71 \times 10^{-8}$  cm.

The angles at which reflection should occur from any other face having the Miller indices ( $h \ k \ l$ ) may now be calculated with the aid of the expression

$$n \lambda = \frac{2 d_{100} \sin \theta}{\sqrt{h^2 + k^2 + l^2}}$$

With the omission of the odd orders from the cube faces, the angles so calculated are given in Tables I and II along with the observed angles.

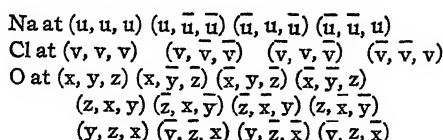
The assumption is made that all of the oxygen atoms occupy equivalent positions in the structure, it is next necessary to consider among the cubic tetartohedral space groups those which give in the most general or in special cases 4, 4, and 12 equivalent positions per unit of structure. There are two space groups which accomplish this, namely, those designated by Schönflies<sup>11</sup>  $T^1$  and  $T^4$ .

<sup>9</sup> See Duane, *Nat. Research Council Bull.*, 1, part 6 (1920).

<sup>10</sup> Groth, "Chemische Krystallographie," Wilhelm Engelmann, Leipzig, 1908, vol. 2, p. 84.

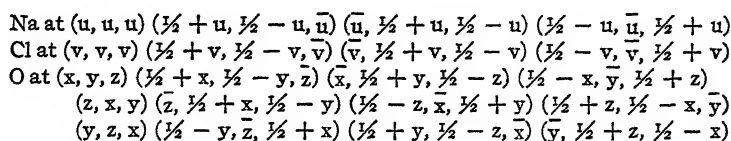
<sup>11</sup> Schönflies, "Krystallsysteme u. Krystalstruktur," Teubner, Leipzig, 1891.

The arrangement of atoms is, according to  $T^1$ ,



The parameters appearing in the coördinates are taken as fractions of  $d_{100}$ . Since the right- and left-handed varieties of a crystal behave in the same manner toward X-rays,<sup>2</sup> it is not possible to choose between two enantiomorphously related structures.

The arrangement of atoms is, according to  $T^4$ ,



No odd orders of reflection were found from the cube faces of either of the substances. Now irrespective of the values of  $u$ ,  $v$ ,  $x$ ,  $y$ , and  $z$ , and of any special assumptions as to the reflecting power of the different atoms, the second arrangement, but not the first, causes all the odd orders of reflection from the cube faces to vanish.

The assumption here made that all the oxygen atoms occupy equivalent positions seems justifiable. For no arrangement with the requisite symmetry and number of sodium chlorate per unit is possible on the assumption that two oxygen atoms are equivalent and the third different; and the assumption that all three oxygen atoms are non-equivalent is improbable. We have therefore adopted the arrangement derived from the space group  $T^4$ .

Completion of the knowledge of the crystal structure requires the determination of the values of the 5 unknown parameters, and this can best be done by a consideration of the intensities of reflection. There seems to be no way of finding the values of these parameters except by trial; and since 5 of them are involved, the number of possibilities is great. In view of the present rather scant knowledge of the mechanism of reflection there is no way of knowing how good agreement to expect between the calculated and observed results. There is, moreover, no assurance that when a satisfactory set of values has been found, another equally good set may not be possible. We have nevertheless determined a set of values of these parameters which leads to a rough agreement between the calculated and observed intensities.

The intensities were calculated with the aid of the expression,  $I = f(\theta)(A^2 + B^2)$ . In this expression,

$$\begin{aligned}
A = & \bar{\text{Na}} \left[ \cos 2\pi n(h+k+l)u + \cos 2\pi n\left(\frac{h+k}{2} + (h-k-l)u\right) \right. \\
& \left. + \cos 2\pi n\left(\frac{k+l}{2} + (-h+k-l)u\right) + \cos 2\pi n\left(\frac{h+l}{2} + (-h-k+l)u\right) \right] \\
& + \bar{\text{Cl}} \left[ \cos 2\pi n(h+k+l)v + \cos 2\pi n\left(\frac{h+k}{2} + (h-k-l)v\right) \right. \\
& \left. + \cos 2\pi n\left(\frac{k+l}{2} + (-h+k-l)v\right) + \cos 2\pi n\left(\frac{h+l}{2} + (-h-k+l)v\right) \right] \\
& + \bar{\text{O}} \left[ \cos 2\pi n(hx+ky+lz) + \cos 2\pi n\left(\frac{h+k}{2} + hx-ky-lz\right) \right. \\
& + \cos 2\pi n\left(\frac{k+l}{2} - hx+ky-lz\right) + \cos 2\pi n\left(\frac{h+l}{2} - hx-ky+lz\right) \\
& + \cos 2\pi n(hz+kx+ly) + \cos 2\pi n\left(\frac{k+l}{2} - hz+kx-ly\right) \\
& + \cos 2\pi n\left(\frac{h+l}{2} - hz-kx+ly\right) + \cos 2\pi n\left(\frac{h+k}{2} + hz-kx-ly\right) \\
& + \cos 2\pi n(hy+kz+lx) + \cos 2\pi n\left(\frac{h+k}{2} - hy-kz-lx\right) \\
& \left. + \cos 2\pi n\left(\frac{h+k}{2} + hy-kz-lx\right) + \cos 2\pi n\left(\frac{k+l}{2} - hy+kz-lx\right) \right]
\end{aligned}$$

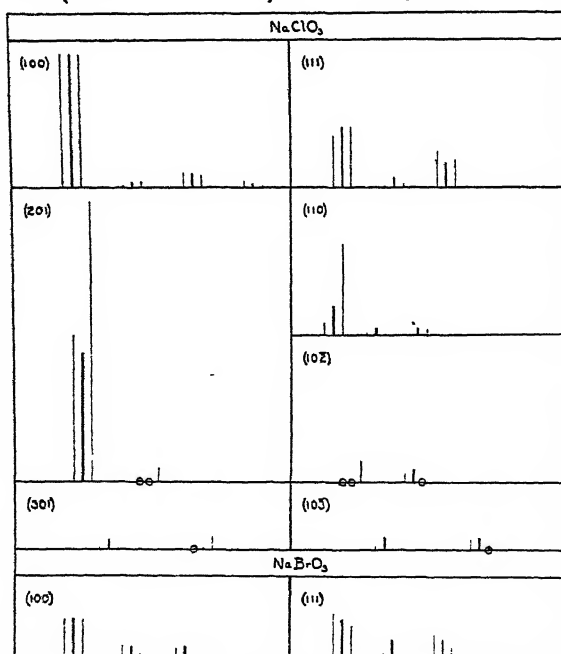


Fig. 1

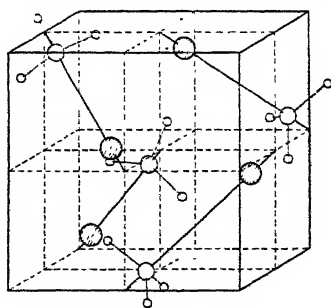
B is a similar expression in sine terms. Here Na, Cl, and O have been taken proportional to the atomic numbers of the respective elements. The relative values of  $f(\theta)$  have been estimated by taking 100:20:5 as the normal ratios for the cube face of sodium chloride, plotting these against  $\sin \theta$ , and drawing an interpolation curve through these points. In order to get a straighter curve, the plot was actually made with the reciprocals of the square roots of the normal intensities against  $\sin \theta$ .

Tables III and IV contain the results of these calculations. The values of the parameters finally chosen are for the chlorate,  $u = 0.08$ ,  $v = 0.43$ ,  $x = 0.30$ ,  $y = 0.59$ ,  $z = 0.47$ ; for the bromate;  $u = 0.09$ ,  $v = 0.41$ ,  $x = 0.30$ ,  $y = 0.60$ ,  $z = 0.47$ . The tables show in the fourth column the observed intensities; in the fifth, the intensities calculated using our values of the parameters; in the sixth, the intensities calculated using the parameters  $u = \frac{5}{12} = (0.083)$ ,  $v = \frac{5}{12} = (0.417)$ ,  $x = \frac{1}{2} = (0.500)$ ,  $y = \frac{5}{12} = (0.417)$ ,  $z = \frac{11}{36} = (0.306)$ , which are those chosen by Kolkmeijer, Bijvoet and Karssen.<sup>3</sup> These three sets of intensities are also shown graphically in Fig. 1. The heavy lines represent the observed intensities. The lighter lines to the left represent the intensities calculated with our parameters, while the light lines to the right represent the intensities calculated with the parameters of Kolkmeijer, Bijvoet and Karssen. Their structure gives as good agreement with our data as our own structure except for faces all of whose indices are different. That any disagreement should appear here, if at all, is not surprising, since powder photographs, from which their structure was derived, do not separate reflections due to (hkl) and (khl).

## 5. Discussion of the Crystal Structures.

Their structure and ours are in substantial agreement as regards the displacement of the sodium and halogen atoms toward each other along diagonals from the positions occupied by these atoms in the sodium halides; and both agree in placing 3 oxygen atoms near a halogen with the halogen nearly in their plane. But their structure orients the oxygen atoms somewhat differently from ours and places them considerably closer to the halogen. Thus the distances between the respective atoms corresponding to their parameters and ours are shown in Table V.

In the last column are shown the distances derived by Bragg's contact-sphere



● Sodium, ○ Halogen; ○ Oxygen

Fig. 2.

principle using his values for the atomic radii.<sup>12</sup> As already pointed out by Kolkmeijer, Bijvoet, and Karssen, their values for the distances between halogen and oxygen are much less than those to which Bragg's atomic radii lead. The difference is seen to be much less in the case of our values, which for the chlorate were deduced before Bragg's paper appeared.

TABLE III.  
CALCULATED INTENSITIES OF REFLECTION FOR SODIUM CHLORATE.

Plane.	Order.	$f(\theta)$ .	Observed intensity.	Calculated intensity. Parameters of D. and G.	Calculated intensity. Parameters of K. B. and K.
(100)	2	135	1.00	(1.00)	(1.00)
	4	30	0.042	0.012	0.043
	6	9.1	0.116	0.117	0.097
	8	3.1	0.033	0.047	0.017
(110)	1	280	0.218	0.096	0.68
	2	66	0.047	0.022	0.004
	3	25	0.052	0.016	0.055
(111)	1	183	0.454	0.383	0.46
(111)	2	42	0.075	0.011	0.036
	3	14	0.181	0.270	0.21
(201)	1	106	0.957	1.10	2.1
	2	22	0.00	0.006	0.11
(10 $\bar{2}$ )	1	106	0.00	0.000	0.16
	2	22	0.097	0.062	0.001
(301)	1	53	0.074	0.017	0.016
	2	7.5	0.017	0.004	0.095
(10 $\bar{3}$ )	1	53	0.088	0.024	0.016
	2	7.5	0.088	0.074	0.000

TABLE IV.  
CALCULATED INTENSITIES OF REFLECTION FOR SODIUM BROMATE.

Plane.	Order.	$f(\theta)$ .	Observed intensity.	Calculated intensity. Parameters of D. and G.	Calculated intensity. Parameters of K. B. and K.
(100)	2	138	0.284	(0.284)	(0.284)
	4	31	0.081	0.093	0.022
	6	9.4	0.081	0.069	0.038
(111)	1	188	0.281	0.321	0.236
	2	44.5	0.133	0.030	0.026
	3	15	0.133	0.163	0.073

TABLE V.  
ATOM DISTANCES.  
Distance in  $10^{-8}$  cm.

Substance.	Atoms.	K. B. and K.	D. and G.	Bragg's radii.
NaClO <sub>3</sub>	Cl to O	0.93	1.43	1.70
	Na to O	2.63	2.41	2.42
NaBrO <sub>3</sub>	Br to O	0.95	1.54	1.84
	Na to O	2.69	2.36	2.42

<sup>12</sup> W. L. Bragg, *Phil. Mag.*, 40, 180 (1920).

The arrangement of the atoms in the unit of structure using our chlorate parameters is shown in Fig. 2.

### Summary.

1. Considerable X-ray spectrometer data for sodium chlorate and a smaller amount for sodium bromate have been collected and tabulated.
2. In agreement with other observers, it has been found that the nature of the crystal surface has a considerable effect on both the absolute and relative intensities of reflection.
3. The ease with which reflections from one face may be mistaken for those from another, and the necessity of precautions to avoid this have been pointed out.
4. It has been shown that the atoms in sodium chlorate and sodium bromate are very probably arranged with the symmetry of the space-group  $T^4$ , all oxygen atoms being equivalent.
5. Sets of locations of the atoms in the unit of structure, only slightly different for the chlorate and bromate, have been suggested.

PASADENA, CALIFORNIA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

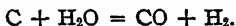
## CATALYSIS IN THE INTERACTION OF CARBON WITH STEAM AND WITH CARBON DIOXIDE.

BY HUGH STOTT TAYLOR AND HARVEY A. NEVILLE.

Received June 20, 1921.

### Introduction.

The interaction of carbon and steam yields, in the first stage of the process, carbon monoxide and hydrogen, according to the equation



In presence of an excess of steam, and especially with suitable catalytic agents, the primary stage may be succeeded by the following reaction.



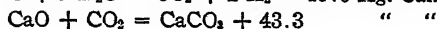
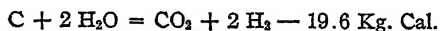
The first equation represents the desired reaction in the steaming phase of blue water-gas preparation. The second occurs to a certain extent, especially as the temperature of the fuel bed is lowered, the ash content of the coke acting as catalytic agent.<sup>1</sup> In the absence of catalytic agents as, for example, with carbon obtained by the thermal decomposition of hydrocarbons, and therefore ash-free, the first reaction takes place practically exclusively. It is evidently, therefore, a faster reaction than the water-gas reaction in the absence of catalytic agents. The second reaction is the principal reaction in the catalytic process for the manufacture of hydrogen from water-gas and steam. Iron oxide is an important con-

<sup>1</sup> Gwosdz, *Z. angew. Chem.*, 31, 137 (1918).

stituent of catalytic agents preferred technically in this process. Since the equation for the water-gas reaction represents an equilibrium which is exothermic in the direction of hydrogen production, it follows that low temperatures and excess of steam favor the elimination of carbon monoxide from the products of the reaction. Temperatures in the neighborhood of 500° are therefore employed in the production of hydrogen by the water-gas catalytic process.

Various attempts have been made to conduct these two reactions in a one-stage technical operation whereby steam is to be passed over carbon of suitable form at a low temperature, so that the reaction products are, in the main, carbon dioxide and hydrogen. To do this efficiently it is necessary to increase the activity of carbon toward steam by the addition of suitable catalytic agents to the reaction mass.

There are a number of patents in existence covering the use of various materials which are to be mixed with charcoal or coke in order to lower the temperature at which the reaction takes place and increase the hydrogen production when the mixture is treated with steam. Among the earliest of these patents is one dated 1867,<sup>2</sup> which proposes the production of hydrogen and carbon dioxide by passing steam over fuel impregnated with lime or caustic soda and heated. Krupp,<sup>3</sup> in a patent of 1892, specifies fuels mixed with hydrates or carbonates. The formation of carbon monoxide is minimized and the carbon dioxide produced is removed by passing over lime. Dieffenbach and Moldenhauer<sup>4</sup> in a series of patents of 1910 suggest the use of coke impregnated or admixed with chlorides, sulfates, or sulfides. Such preparations are stated to be sufficiently active at 600°. With a silicate as catalyst a temperature as high as 750° is used. One of the patents recommends pulverizing the materials, mixing intimately, and briquetting the powdered mixture. It is here claimed that the concentration of carbon monoxide does not exceed a few tenths of 1% when operating at the low temperatures stated. Another patent<sup>5</sup> recommends the admixture of lime in addition to the catalytic agent, in order to absorb the carbon dioxide as it is produced, and thus lower still further the carbon monoxide concentration. A particular preparation mentioned consists of coke impregnated with a 10% potassium carbonate solution and mixed with 5 times its weight of lime, the interval of the reaction temperature being 550–750°. The formation of calcium carbonate is of advantage as the reaction is strongly exothermic and the net thermal effect is therefore positive.



<sup>2</sup> Tessie du Motay and Marechal, Brit. pat. 2548, 1867.

<sup>3</sup> Krupp, Brit. pat. 8426, 1892.

<sup>4</sup> Dieffenbach and Moldenhauer, Brit. pat. 7718, 7719, 7720, 1910.

<sup>5</sup> Dieffenbach and Moldenhauer, Brit. pat. 8734, 1910.



For this reason the duration of steam passage for a given temperature of fuel-bed could be increased.

According to the most recent data,<sup>6</sup> the dissociation pressure of calcium carbonate at 750° is 68 mm. Since the partial pressure of carbon dioxide in the gaseous product would be one-third of an atmosphere, or 253 mm., (assuming the process conducted at atmospheric pressure) if all the steam were converted to hydrogen and carbon dioxide, the lime would, in this case, remove 73% of the carbon dioxide present in the issuing gas. However, there is always an excess of steam, and the partial pressure of carbon dioxide is always less than 253 mm., and hence a smaller percentage is always removed. When the partial pressure of the carbon dioxide falls to 68 mm., none is removed. This will be the case when about 4 times as much steam as will react is being used or, in other words, when a 25% conversion of steam to hydrogen is being obtained. It is thus apparent that the use of lime for the purpose stated cannot be of considerable consequence, unless temperatures in the neighborhood of 550° are used. Since the dissociation pressure of calcium carbonate is only 0.57 mm. at this temperature, a 99% absorption would be attained with a 25% conversion efficiency.

In another list of patents, steam and carbon monoxide, or gases containing it, are passed over coke mixed with metallic oxides and alkalis.<sup>7</sup> Catalysts consisting of metallic couples,<sup>8</sup> such as copper-iron, are also mentioned. Increased pressure is advocated in some cases. For instance, it is stated<sup>9</sup> that, with the use of lime and charcoal, almost pure hydrogen is produced by using steam at ten atmospheres pressure.

Prins,<sup>10</sup> in a patent of 1917, has stated in a more general way the catalysts to be employed in the reaction of steam on carbon. Two or more catalytic agents are to be chosen, one or more from each of the following groups: (a) oxygen-containing salts of the alkali or alkaline-earth metals; (b) inorganic oxides or hydroxides which behave as non-volatile, weak acids or acid anhydrides, as, for example, boric oxide, aluminum oxide, silicon dioxide. Oxides of iron, chromium, and manganese may also be incorporated, doubtless for the purpose of promoting the water-gas reaction which is the second stage of the process, as was previously pointed out. The specified temperature varies from 300° to 600°. The following mixture, for instance, is stated to be efficient at 400–500°: tricalcium orthophosphate, 1 part; silicon dioxide, 2 parts; coke, 20 parts.

It is apparent that there is in the foregoing statements no information

<sup>6</sup> John Johnston, *THIS JOURNAL*, 32, 938 (1910).

<sup>7</sup> Fr. pat. 375164, 459918. Brit. pat. 26770, 1912.

<sup>8</sup> Brit. pat. 6477, 1914.

<sup>9</sup> Ger. pat. 284816. U. S. pat. 1173417.

<sup>10</sup> Prins, Brit. pat. 128273, 1917.

which would indicate the relative merits of the proposed catalysts, the optimum concentration of these, or the effect of temperature change upon the reactions. Neither is there any suggestion of the nature of the mechanism of the catalysis. It was therefore decided in this research to gain some knowledge upon these points by a systematic study of various catalytic agents in their influence upon the reactions. This study has led to a wholly unexpected development of the program of work, since the mechanism of the acceleration by catalytic agents is quite other than was anticipated at the outset.

Many agents were found to catalyze the steam-carbon reaction of which the best were the carbonates of potassium and sodium. With the idea that their influence was to be ascribed to an acceleration of the water-gas reaction,  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , this being known to be slower than the steam-carbon reaction in the absence of catalysts; known good catalysts for the water-gas reaction, for example, iron oxide, were tried as catalysts for the steam-carbon reaction. Iron oxide was found to be quite inactive in this respect, and it was evident, therefore, that another explanation of the mechanism must be sought.

As a possible explanation of the observed catalytic effect in the steam-carbon reaction, it occurred to us that the interaction of carbon dioxide and carbon might be facilitated by the catalytic agents in question and that this was the key to the mechanism of the former reaction. For, if such were the case, the carbon dioxide produced in the second stage of the steaming process,  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , would then interact with carbon to form monoxide,  $\text{CO}_2 + \text{C} = 2\text{CO}$ , which gas, in the presence of the excess of steam, would react as above to form additional quantities of carbon dioxide and hydrogen, thus increasing the net yield of gas from the steam reaction. Experimental tests of this idea showed a complete parallelism between the catalytic effects in the two reactions. In this case reduced nickel was the only catalyst found by us to be superior to the alkali carbonates as accelerating agent, and investigation showed that the low activity of nickel in the steam-carbon reaction was due to a condition brought about by a side reaction, as will be described later. Poor catalysts in the steam-carbon reaction were found to be poor catalysts in the carbon dioxide-carbon reaction, and no material would catalyze this reaction which was not also active in the former case.

As an explanation of the catalytic effect in the carbon dioxide-carbon reaction, it was shown that a mechanism involving alternate reduction and reformation of the alkali carbonates was not correct. These experiments, however, led us to make a determination of the adsorption capacity of carbon for carbon dioxide at the reaction temperatures concerned, both when alone and when impregnated with various catalytic agents. The results of these experiments showed in a striking manner that good catalysts

for both of the reactions under investigation also caused a marked increase in the adsorptive capacity of carbon for carbon dioxide as measured at 445°. Our experiments have indicated that this increased adsorption of carbon dioxide by carbon may be attributed to the action of the catalytic agents in facilitating the decomposition of "fixed oxygen" complexes on the carbon surface, thus cleaning the surface to an extent which would ordinarily only be attained by subjecting the carbon to considerably higher temperatures.<sup>11</sup> Definite evidence has also been obtained that such inactive oxygen complexes may be partially broken down into carbon monoxide and carbon dioxide by prolonged heating at the temperature of the experiments, even in absence of catalytic agents, and that they may be reformed by carbon dioxide under these conditions.

## II. Experimental.

**Materials.**—The form of carbon most extensively studied in this investigation was a coconut-shell charcoal produced in large quantities during the recent war for use in gas masks, and officially known as A909. This charcoal was prepared from coconut shells by carbonization at 950° for 10 hours, followed by steam activation at 950° for 45 minutes.<sup>12</sup> The sample used was passed through an 18-mesh screen and the finer powder removed. The true density of this charcoal was found to be 1.84.<sup>13</sup>

Other forms of carbon used were: (1) sugar charcoal, made by dehydrating recrystallized cane sugar with conc. sulfuric acid, subsequent washing free from acid and heating to dull redness; (2) a high-temperature coke; (3) kelp-char, containing 2.2% of alkali carbonates, calculated as sodium carbonate, which could be extracted with hot water; (4) a retort carbon furnished by the DuPont Company, containing 1.8% of sodium carbonate, determined as above.

The catalysts employed, in the case of salts, were the pure anhydrous compounds. A charge was prepared as follows. The carbon and the catalyst in weighed proportions were moistened with water, mixed thoroughly, and then heated until dry. In this way the catalyst was deposited on the surface and in the pores of the charcoal in a finely divided form, and in intimate contact with the carbon. When reduced nickel was used as catalyst, the desired amount was weighed out as tetrahydrated nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), dissolved in water and the charcoal moistened with the solution. This mixture was then dried and heated to decompose the nitrate, leaving the oxide of nickel on the surface of the charcoal. The sample was then placed in the reaction tube and reduced *in situ* with hydrogen at the temperature at which it was to be used, that is, 570°. A charge consisted of 8 g. of charcoal plus an amount of the catalyst calculated as a certain percentage of the total weight. For example, A909 plus 20% of potassium carbonate refers to 8 g. of the char mixed with 2 g. of anhydrous potassium carbonate.

**Apparatus.**—The apparatus used to study the reaction of steam upon carbon was essentially as shown in Fig. 1. It was constructed entirely of Pyrex glass. The internal diameter of the reaction tube was 1.6 cm., and the charge occupied a length of 11 cm. The thermocouple in its sheath was inserted so that its end was at the middle point of the charge. It was made of Hoskins base metal alloys (No. 183 vs. 343; 343 pos.) and was calibrated at several points between 100° and 658°. The temperature was measured

<sup>11</sup> Lowry and Hulett, *THIS JOURNAL*, 42, 1408 (1920).

<sup>12</sup> Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, 11, 420 (1919).

<sup>13</sup> Cude and Hulett, *THIS JOURNAL*, 42, 391 (1920).

by means of a pyrovoltmeter made by the Pyroelectric Company, the accuracy being well within  $\pm 5^\circ$  and the relative variations probably much less. The two joints of the apparatus were made securely gas-tight by wrapping them with rubber dam. The portion of the apparatus extending out of the furnace was wound with resistance wire

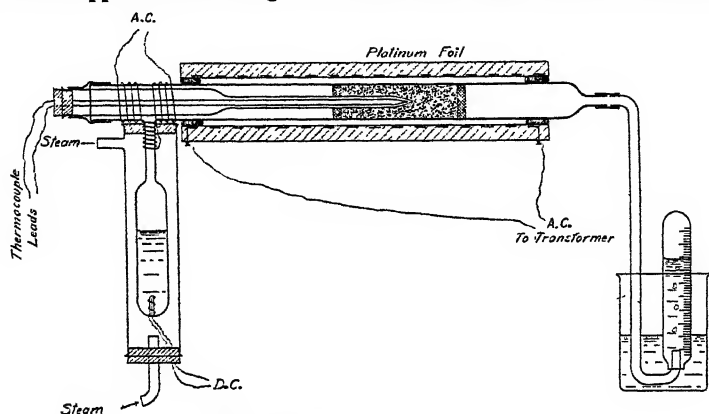


Fig. 1.—Diagram of apparatus.

and heated to prevent condensation of the steam. This steam was generated electrically as shown in the figure. A current of steam was passed through the outer jacket of this generator in order to bring the contents to  $100^\circ$ . Inside, was a platinum spiral of known resistance with leads fused through the glass. This was heated by a constant direct

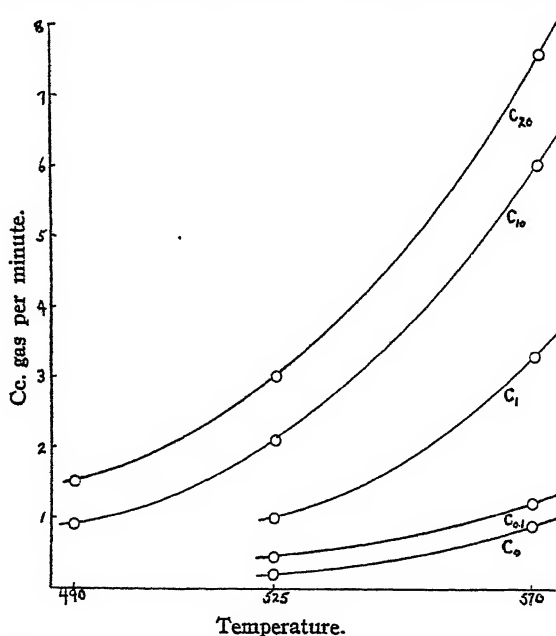


Fig. 2.—Amount of gas produced with different percentages of sodium carbonate.

current to convert the water at 100° to steam. The rate of steam passage per minute could be calculated from the relation

$$H = 0.24 I^2 R t = 64.08 \text{ calories,}$$

where  $H$  is the number of calories of heat produced;  $I$ , the current (1 ampere);  $R$ , the resistance of the spiral at 100° (4.45 ohms);  $t$ , the time (60 seconds); and 0.24, the heat equivalent of electrical energy. The heat of vaporization of water at 100° is 538 cal.;  $64.08/538 = 0.1191$  g. of water vaporized per minute, which corresponds to 148 cc. at 0° and 760 mm. pressure, and to 160 cc. at 20° and 760 mm.

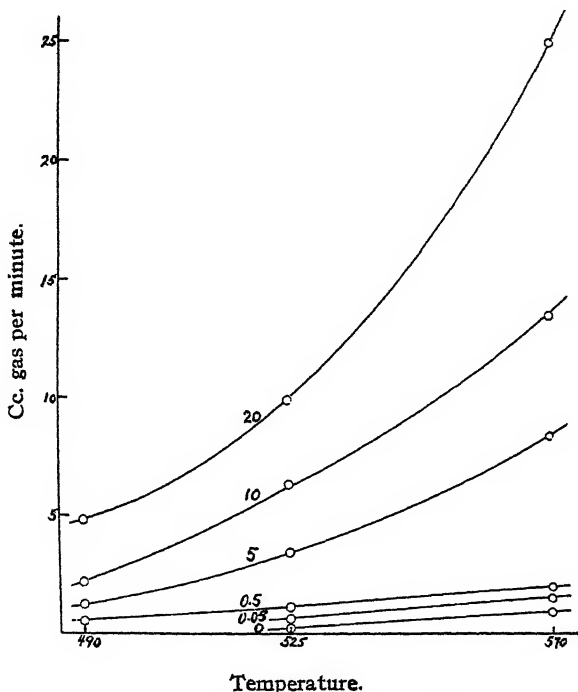


Fig. 3.—Amount of gas produced with different percentages of potassium carbonate.

In studying the reaction of carbon dioxide upon the charcoal, a reaction tube similar to the one shown in Fig. 1 was used, with the exception that the steam generator was replaced by a side tube through which carbon dioxide was introduced. The carbon dioxide was obtained from a tank of the liquefied gas. Its rate of passage was measured by a flow-meter which had been previously calibrated for this gas. A constant pressure of carbon dioxide through the system was maintained by means of a blow-off through a side tube extending into an adjustable height of water. The gases issuing from this reaction were collected over caustic potash solution in order to absorb the carbon dioxide which had not been reduced. The residual gas was practically pure carbon monoxide, containing a small amount of hydrogen, due either to a trace of moisture in the carbon dioxide or in the charcoal, or obtained by further decomposition of hydrocarbons not removed from the char in its preparation.

### III. Experimental Results.

**Steam on Carbon.**—The temperatures chosen for this study were conveniently 490°, 525° and 570°. Below 490° the reaction was too slight to be appreciable in most cases, and above 570° the reaction tube softened.

As a basis for comparison, an experiment was carried out without any catalyst. This was followed by experiments on charcoal moistened with solutions of barium hydroxide, water glass, borax, soda-lime, sodium and potassium carbonates. The last two substances, only, showed a considerable catalytic effect. These two alkali carbonates were subsequently studied as catalysts in detail, in addition to a number of other substances.

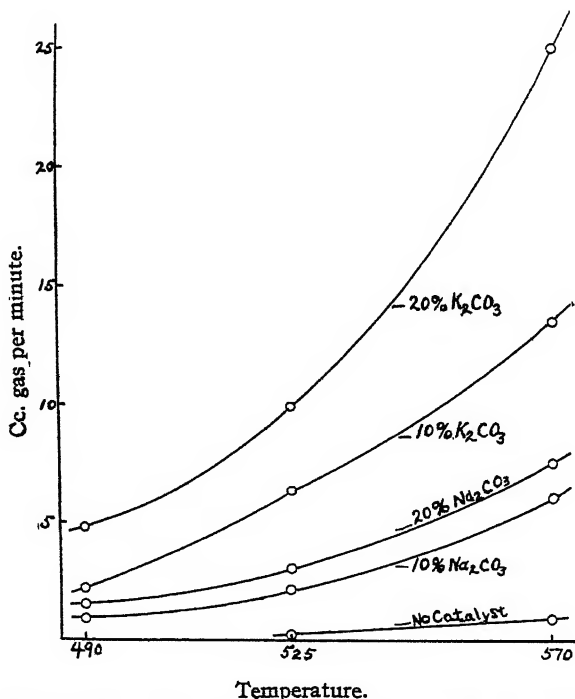


Fig. 4.—Comparison of K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>. Reaction  
 $C + 2H_2O = CO_2 + 2H_2$ .

The results are shown in the accompanying Table I. The data on sodium and potassium carbonates are graphically represented in Figs. 2, 3, 4 and 5. The effect upon the reaction of variations in the temperature and in the amount of catalytic agent employed is clearly indicated in these curves. The results here recorded were obtained by passing steam at a constant rate of 160 cc. per minute over 8 g. of charcoal plus the catalyst, prepared as described above. The rate of production of gas was measured in cubic centimeters per minute at 20° and 760 mm. pressure, and was taken

as an indication of the relative rate of the reaction in each case. The gases were collected over dil. sulfuric acid and were completely analyzed. Their composition usually approximated a mixture of two volumes of hydrogen and one volume of carbon dioxide, in agreement with the relation  $C + 2H_2O = CO_2 + 2H_2$ . When there was a deviation from this ratio it could be explained. For example, when using lithium, calcium or barium carbonate as catalyst, the proportion of carbon dioxide was too great, owing to dissociation of the carbonate. When an oxidizing agent like sodium nitrate was used, too much carbon dioxide was found in the

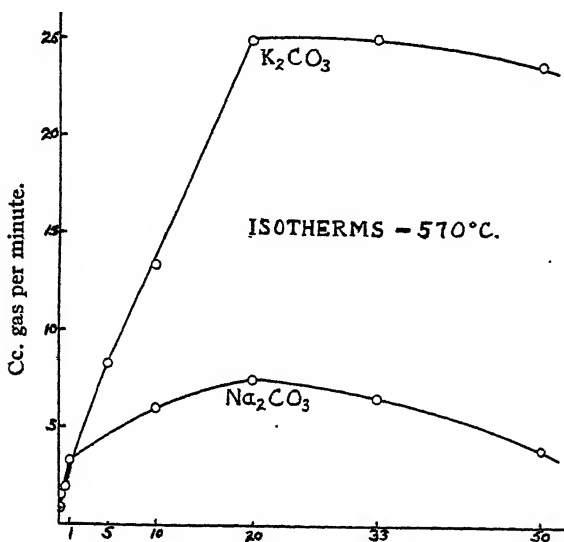


Fig. 5.—Concentration of catalyst in percentages.

product because oxidation of the carbon or removal of hydrogen by oxidation had occurred. In this instance, some oxygen also was found.

The presence of carbon monoxide in the reaction product could hardly ever be detected with our gas-analysis apparatus, as the amount present in a 20cc. sample was usually less than 0.05 cc. The theoretical concentration of carbon monoxide at any temperature can be calculated from the water-gas equilibrium,  $CO + H_2O \rightleftharpoons CO_2 + H_2$ .

At equilibrium,

$$\frac{C_{H_2O} \times C_{CO}}{C_{H_2} \times C_{CO_2}} = K = 0.25 \text{ at } 600^\circ.$$

With steam passing at the rate of 160 cc. per minute, and gas being produced at the rate of 6 cc. per minute, taking into account the fact that  $\frac{2}{3}$  cc. of steam disappears for every cubic centimeter of gas produced, the equation becomes

$$\frac{155.3 \times C_{\text{Co}}}{4 \times 2} = 0.25.$$

Hence the production of carbon monoxide is at the rate of 0.013 cc. per minute, which represents 0.21% of the gas mixture. When gas is produced at the rate of 25 cc. per minute (cf. A909 + 20%  $\text{K}_2\text{CO}_3$ ) the quantity of carbon monoxide becomes 0.24 cc. per minute or 0.96% of the gaseous product.

TABLE I.

Material. % Catalyst.	Cc. gas per minute.		
	At 490°.	At 525°.	At 570°.
A909(8 g.).....	0	0.2	0.9
0.05 $\text{K}_2\text{CO}_3$ .....	0	0.6	1.5
0.5 $\text{K}_2\text{CO}_3$ .....	0.5	1.1	2.0
5 $\text{K}_2\text{CO}_3$ .....	1.2	3.4	8.4
10 $\text{K}_2\text{CO}_3$ .....	2.2	6.3	13.5
20 $\text{K}_2\text{CO}_3$ .....	4.8	9.9	25.0
33 $\text{K}_2\text{CO}_3$ .....	4.7	9.3	25.1
50 $\text{K}_2\text{CO}_3$ .....	5.0	10.0	23.8
10 $\text{Na}_2\text{CO}_3$ .....	0.9	2.1	6.0
20 $\text{Na}_2\text{CO}_3$ .....	1.5	3.0	7.5
33 $\text{Na}_2\text{CO}_3$ .....	0.7	1.8	6.7
50 $\text{Na}_2\text{CO}_3$ .....	...	1.0	4.0
10 $\text{K}_2\text{CO}_3$ .....	5.1	10.6	24.0
10 $\text{Na}_2\text{CO}_3$ .....			
5 $\text{K}_2\text{CO}_3$ .....	2.1	4.9	13.4
15 $\text{Na}_2\text{CO}_3$ .....			
20 $\text{Li}_2\text{CO}_3$ .....	0.4	1.2	4.1
20 $\text{BaCO}_3$ .....	...	0.4	1.3
20 $\text{CaCO}_3$ .....	0.2	..	1.1
20 $\text{NaCl}$ .....	0.2	0.5	1.9
10 $\text{Fe}_2\text{O}_3$ .....	...	0.3	0.9
20 $\text{Cu}$ .....	...	0.6	1.4
10 Water Glass.....	...	..	1.0
10 Borax.....	...	1.3	...
Kelp char			
10 $\text{Na}_2\text{CO}_3$ .....	1.2	4.0	18.0
Coke			
20 $\text{K}_2\text{CO}_3$ .....	0.4	1.2	5.0
Sugar charcoal			
20 $\text{K}_2\text{CO}_3$ .....	3.4	7.5	21.0
DuPont charcoal			
20 $\text{K}_2\text{CO}_3$ .....	2.8	6.3	16.8

The data recorded in Table I make apparent the following facts. (1) Of the materials studied, potassium and sodium carbonates are the only efficient catalysts for the reaction, and potassium carbonate is about three times as active in this respect as the sodium salt. (2) Other salts of the alkalies and alkaline earths have a slight catalytic effect. (3) Iron oxide exerts no influence whatever.



Since it is almost certain that the reaction progresses in two stages, (a)  $C + H_2O = CO + H_2$ ; (b)  $CO + H_2O = CO_2 + H_2$ ;  $C + 2H_2O = CO_2 + 2H_2$ , and since iron oxide is a very good catalyst for Reaction b, it may be concluded that first, the water-gas reaction attains its equilibrium under the conditions of these experiments, even in the absence of such substances as iron oxide; and second, the observed catalysis of the reaction between steam and carbon cannot be due to a catalysis of the water-gas reaction but must be due to an acceleration of the first stage or of some other reaction concerned. The catalysis of the reaction,  $C + CO_2 = 2CO$ , satisfies these conditions and is considered sufficient to account for the increased production of gas when catalytic agents are used in the steam-carbon process.

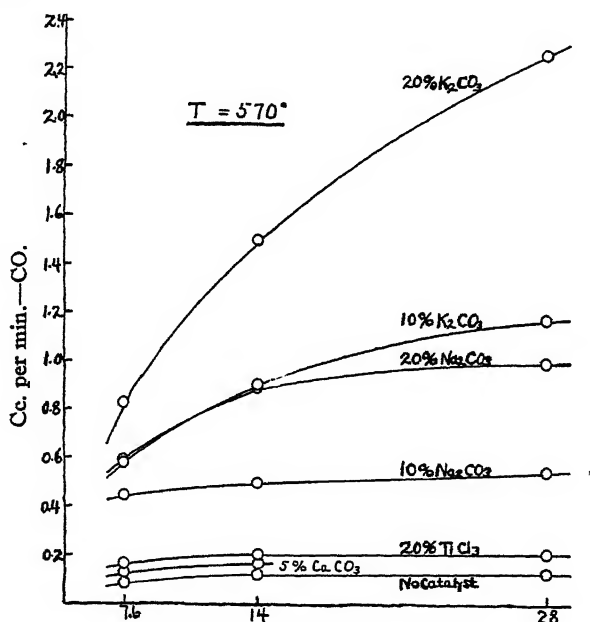


Fig. 6.—Rate of  $CO_2$ . Cc. per min.

Charcoal, containing reduced nickel incorporated in the manner previously described, when treated with steam at  $570^\circ$ , produced gas at the rate of 80 cc. per minute at the beginning of the operation. After an hour's passage of steam, the rate of evolution of gas had fallen to 6 cc. per minute. It was thought that the decrease in the activity of the nickel as catalyst might be due to surface oxidation by the steam. If this were the case, it should recover its activity when again reduced with hydrogen. The steam generation was stopped and a stream of hydrogen was substituted for it. When steam was again passed through the charge, the evolution of gas was at the rate of 4 cc. per minute, and fell during an hour to an

apparently constant value at 2.6 cc. per minute. It is probable that the nickel had either become coated over with a deposit of carbon due to decomposition of carbon monoxide, a reaction catalyzed by nickel, or that it had been agglomerated, by being heated at  $570^{\circ}$  for a considerable time, into larger particles which had much less catalytic activity.

**Carbon Dioxide on Carbon.**—Materials similar to those studied in the preceding steam-carbon reaction were used as catalysts for this reaction. The results of these experiments are recorded in Table II and graphically represented in Fig. 6. From a comparison of the values given in the two tables, it is evident that the activities of the catalytic agents are in the same order in the two reactions. These experiments were all carried out at  $570^{\circ}$ , but the rate of passage of carbon dioxide was varied. An excess of an inactive catalyst such as calcium carbonate mixed with the charcoal produced a more decided protective effect than was observed in the steam-carbon reaction. In the latter case, the velocity of the gas (160 cc. per minute) through the apparatus was from 5 to 20 times as great and, therefore, the turbulent motion of its molecules was less impaired than in the case of the slower stream of carbon dioxide. The two experiments with nickel as catalyst, using respectively 7.5 and 20% of the metal, gave almost identical results, indicating that the optimum concentration of catalytic agent was already reached in the first instance.

TABLE II.  
A909 TREATED WITH  $\text{CO}_2$  AT  $570^{\circ}$ .

Rate of $\text{CO}_2$ , Cc./min.	7.6	14.0	28.0
Material.	CO. Cc./min.	CO. Cc./min.	CO. Cc./min.
% Catalyst.			
A909 (8g.)	0.086	0.124	0.137
20 $\text{Fe}_2\text{O}_3$ .....		Protective effect	
5 $\text{Fe}_2\text{O}_3$ .....		No effect	
20 $\text{CaCO}_3$ .....		Protective effect	
5 $\text{CaCO}_3$ .....	0.133	0.17	..
20 $\text{K}_2\text{CO}_3$ .....	0.833	1.50	2.27
10 $\text{K}_2\text{CO}_3$ .....	0.58	0.91	1.18
20 $\text{Na}_2\text{CO}_3$ .....	0.60	0.92	1.00
20 $\text{NaCl}$ .....	0.15	0.20	0.24
7.5 Ni.....	2.3	4.1	7.7
20 Ni.....	2.0	4.1	7.8

The decomposition of carbon monoxide into carbon dioxide and carbon, as was mentioned earlier, was known to be catalyzed by reduced nickel. It was, therefore, to be expected that nickel would catalyze the reverse reaction,  $\text{C} + \text{CO}_2 = 2\text{CO}$ . Reference to Table II will show that it was by far the best catalyst found. Furthermore, it did not lose its activity as it did in the steam-carbon reaction. The large excess of carbon dioxide in the present instance, no doubt, prevented the reverse reaction from being considerable.

It was supposed by H. St.-Claire Deville, who first observed the decomposition of carbon monoxide, that the decomposition would increase with rise in temperature.<sup>14</sup> However, since the reaction is exothermic,  $2 \text{ CO} = \text{CO}_2 + \text{C} + 39 \text{ kg. cal.}$ , according to the van't Hoff principle of mobile equilibrium, the quantity of carbon monoxide present in equilibrium with carbon dioxide and carbon will decrease as the temperature is lowered. Boudouard's results<sup>15</sup> for this equilibrium are, 0, 39.0 and 93.4% of carbon monoxide remaining at 445°, 650° and 800° respectively. Rhead and Wheeler<sup>16</sup> found figures substantially in agreement with Boudouard at the higher temperatures by heating carbon in an atmosphere of carbon dioxide, namely 93.77 and 97.78% of carbon monoxide formed at 850° and 900°, respectively. They also noted that the reaction  $\text{C} + \text{CO}_2 = 2 \text{ CO}$ , proceeded 166 times as fast as the reverse reaction at 850°.

Following Boudouard's conclusion that carbon monoxide is metastable at 445°, Smits and Wolff undertook to determine the velocity of the decomposition,  $2 \text{ CO} = \text{CO}_2 + \text{C}$ , in the metastable range, using finely divided nickel as catalyst.<sup>17</sup> They found the reaction to be monomolecular, and assumed that it occurred in two phases: (1)  $\text{CO} = \text{C} + \text{O}$ , with measurable velocity; and (2)  $\text{CO} + \text{O} = \text{CO}_2$  with immeasurably great velocity. They determined that the reaction, in contradiction to the work of Boudouard, was very distinctly reversible at 445°, but found no satisfactory value for the equilibrium constant. The incompleteness of decomposition of carbon monoxide at 445°, as indicated in this research is of importance in reference to the value of 23.15% of carbon monoxide obtained by us in the experiment cited below. These values suggest the necessity of a careful restudy of the equilibrium,  $\text{CO}_2 + \text{C} \rightleftharpoons 2 \text{ CO}$ , in the interval 445–800°.

Briner and Wroczynski<sup>18</sup> found that, in agreement with the Le Chatelier theorem, the decomposition of carbon monoxide was favored by increased pressure. Rhead and Wheeler corroborate this in a later paper,<sup>19</sup> and apply a formula to calculate the ratio  $\text{CO}/\text{CO}_2$  at any temperature and pressure:

$$\frac{38055 + 2.02 T - 0.0031 T^2}{2 T} + \ln P + \ln \frac{C_1}{C_2} = K = 18.75.$$

In the present investigation, when carbon dioxide was passed at a very slow rate over carbon coated with 7.5% reduced nickel at 570°, the resulting gas, collected over mercury and analyzed, was found to contain 23.15%

<sup>14</sup> Deville, *Compt. rend.*, 59, 873 (1889); 60, 317 (1890).

<sup>15</sup> Boudouard, *ibid.*, 128, 822, 1522 (1899); *Ann. chim. phys.*, 7, 24 (1901).

<sup>16</sup> Rhead and Wheeler, *J. Chem. Soc.*, 97, 2178 (1909).

<sup>17</sup> Smits and Wolff, *Z. physik. Chem.*, 45, 199 (1903).

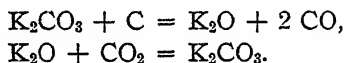
<sup>18</sup> Briner and Wroczynski, *Compt. rend.*, 150, 1324 (1910).

<sup>19</sup> Rhead and Wheeler, *J. Chem. Soc.*, 99, 1140 (1911).

of carbon monoxide. This was the average of 6 analyses which were in close agreement among themselves. As calculated by means of the above formula, the pressure being one atmosphere and, therefore, the middle term dropping out, the concentration of carbon monoxide at 570° should be 17.3%.

Upon the principle that the catalyst for a reaction should also catalyze the reverse reaction, it was attempted to show that potassium carbonate would accelerate the decomposition of carbon monoxide. A stream of carbon monoxide which had been purified and dried was passed at a constant rate of 10 cc. per minute over a charge of charcoal at 570° and the resulting gas was analyzed. The experiment was repeated with the addition of 20% of potassium carbonate to the charcoal. The first analysis showed that 19% of the carbon monoxide had been converted to carbon monoxide and carbon and, in the second case, the decomposition amounted to 29%. A catalytic effect is hereby demonstrated, and evidently the reasoning is orthodox.

**Heating Charcoal with the Catalyst.**—The idea that the catalysis of the reaction,  $C + CO_2 = 2 CO$ , was due to alternate reduction and re-formation of the alkali carbonates was suggested as a possible mechanism of the reaction. This might occur as follows.



This view was shown to be incorrect by heating some charcoal in an atmosphere of nitrogen, both alone and with 20% of potassium carbonate. The gases evolved during the heating were of the same composition (*ca.* 15% CO and 85% CO<sub>2</sub>) in each case, though a somewhat larger amount came off when the catalyst was present. Especially was it true that the gases came off more rapidly when the potassium carbonate was used than when the carbon was heated alone. The gases were presumably due to the decomposition of the surface complex of "fixed oxygen," or C<sub>x</sub>O<sub>y</sub>, described by Rhead and Wheeler,<sup>20</sup> and recently studied by Lowry and Hulett.<sup>11</sup> These facts seem to indicate that the surface compound may be more readily removed in the presence of substances such as potassium carbonate and that the cleaned surface is then more reactive toward carbon dioxide. If this be true, then the activity of the charcoal alone ought to be much greater after prolonged heating than at first, as a certain amount of the gases is removed finally, even in absence of potassium carbonate. This is correct to some extent, for the reaction of the charcoal with carbon dioxide is considerably greater after a period of heating when no gas is being passed than before, but very soon falls to exactly its original

<sup>20</sup> Rhead and Wheeler, *J. Chem. Soc.*, 103, 461 (1912).

activity after the passage of carbon dioxide has been resumed.<sup>21</sup> These results apparently indicate that carbon dioxide is able to reform the surface complex,  $C_xO_y$ , or that the gas is adsorbed in some intimate way and changes the reactivity of the carbon.

Rhead and Wheeler state<sup>20</sup> that the oxidation of carbon always consists in the formation of the indefinite oxygen-carbon complex and that this subsequently decomposes into carbon monoxide and carbon dioxide, since both these gases are shown to be primary products in the combustion of carbon. Hence it would appear that the oxidation of carbon by carbon dioxide must take place in some such manner. If carbon can take up carbon dioxide to form  $C_xO_y$ , and this complex then decompose to give carbon monoxide and carbon dioxide in a ratio dependent upon the temperature, and if such substances as potassium carbonate can catalyze these reactions, then we have a mechanism which explains the catalysis of the reaction,  $C + CO_2 = 2 CO$ , and consequently the catalysis of the reaction,  $C + 2 H_2O = CO_2 + 2 H_2$ .

**Adsorption of Carbon Dioxide.**—Whether or not a surface oxide is formed and decomposed in the manner indicated cannot be definitely stated. It is, however, certain that the presence in the carbon of such substances as potassium carbonate increases the concentration of carbon dioxide on the surface of the charcoal. This effect is more marked at temperatures higher than those at which adsorption ordinarily plays a part, and this is consistent with the fact that the specific catalytic effect of the same substances increases with temperature. We are inclined to regard such factors as strong presumptive evidence of a  $C-CO_2$  complex formation.

Table III gives a comparison of the catalytic effect of several substances

<sup>21</sup> Effect of heating the char. Eight g. of A909 was heated for 20 hours at 570°. The system was then washed out with  $CO_2$  for 10 minutes.

Passing  $CO_2$  at the rate of 14 cc./min., samples were collected successively.

	Time. Min.	CO produced. Cc.	CO per min. Cc.
(1)	21	13	0.62
(2)	20	8.5	0.425
(3)	35	7.5	0.21
(4)	60	9.5	0.16

Passage of  $CO_2$  was stopped, heating was continued at 570° for 17 hours.

Passing  $CO_2$  again at 14 cc./min. a sample was collected giving

(5)	2.5	20	8.0
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The system was washed out with  $CO_2$  for 15 minutes. Samples then collected.

(6)	15	5	0.33
(7)	30	6.5	0.22
(8)	40	7.0	0.17

After three hours with  $CO_2$  passing continuously at 14 cc./min., a sample was taken.

(9)	30	3.7	0.123
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This final value agrees with that given in Table II (0.124 cc./min.) obtained by the usual procedure of bringing the charge to 570° in about 2 hours, with  $CO_2$  passing through the system continuously.

upon the two reactions with their effect upon the adsorptive capacity of charcoal for carbon dioxide. The adsorption measurements were made by means of the apparatus described by Taylor and Burns.<sup>22</sup> The adsorption capacity of reduced nickel for carbon dioxide at 445° was there reported to be negligible. The adsorption on pure potassium carbonate at this temperature was also tested in the present experiments and was found to be practically nil.

TABLE III.

	Catalyst. %.	Interaction of C and H <sub>2</sub> O at 570°.	Interaction of C and CO <sub>2</sub> at 570°.	Adsorption of CO <sub>2</sub> per g. of C. at 445°.
		Gas produced. Cc./min.	Gas produced. Cc./min.	Cc.
20	K <sub>2</sub> CO <sub>3</sub> .....	25	2.3	4.4
20	Na <sub>2</sub> CO <sub>3</sub> .....	7.5	1.0	2.0
7.5	Ni.....	2.6 (final value)	7.7	1.76
20	NaCl.....	1.8	0.24	0.4
	No Catalyst.....	0.9	0.14	0.33

In the above table the only substance exhibiting anomalous behavior is reduced nickel. Its activity in the carbon dioxide-carbon reaction is above that of the other catalysts, but its effect upon the adsorptive capacity of carbon falls below that of the alkali carbonates. Its irregularity in the steam-carbon reaction was previously noted and discussed; the reason for its loss in activity in that case may also be applicable here.

There is a possibility, in favor of which however no evidence is as yet forthcoming, that steam might also be "fixed" on a carbon surface just as carbon dioxide is; that, moreover, catalytic agents such as potassium carbonate might in such case also bring about an increase in the concentration of steam on the charcoal surface. The experimental method of testing this possibility would not be simple since chemical reaction, to yield hydrogen and carbon monoxide, would occur in part. Furthermore, the technique of adsorption measurements with steam requires extended development before such a viewpoint can be satisfactorily taken.

#### IV. Summary.

1. The effect of certain catalytic agents upon the interaction of steam and carbon has been studied, using various forms of carbon.
2. It has been discovered that the interaction of carbon dioxide and carbon is likewise accelerated by the presence of the same materials, and a striking parallelism between the catalysts for the two reactions has been demonstrated.
3. The probable mechanism of the steam-carbon reaction has been investigated.
4. It has been shown that good catalysts for the water-gas reaction, for example, iron oxide, are ineffective in the steam-carbon and carbon dioxide-carbon reactions.

<sup>22</sup> Taylor and Burns, *THIS JOURNAL*, 43, 1273 (1921).

5. Catalysis of the water-gas reaction thus being excluded from consideration, it has been shown that the acceleration of the reaction  $C + CO_2 = 2 CO$ , and therefore the acceleration of the reaction,  $C + 2 H_2O = CO_2 + 2 H_2$ , may be ascribed to increased adsorption of carbon dioxide by the carbon surfaces in presence of active catalytic agents.

6. Adsorption measurements have been shown to confirm this view.

7. The results obtained have been considered in view of the proposed existence of a surface complex  $C_xO_y$ , and have been found to agree with this conception.

The authors of this paper wish hereby to thank Dr. R. M. Burns for his assistance in the adsorption measurements.

This research was carried out while Mr. Neville was the DuPont Fellow in Princeton; and it is desired to express to the DuPont Company an appreciation of their aid.

PRINCETON, NEW JERSEY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NOTRE DAME.]

## THE ROLE OF MERCURY SALTS IN THE CATALYTIC TRANSFORMATION OF ACETYLENE INTO ACETALDEHYDE, AND A NEW COMMERCIAL PROCESS FOR THE MANUFACTURE OF PARALDEHYDE.

BY RICHARD R. VOGT AND JULIUS A. NIEUWLAND.

Received April 28, 1921.

It is well known that acetaldehyde can be prepared commercially from acetylene and water by the use of mercury salts as catalysts. A drawback to the process lies in the ease with which the mercury salt is reduced to the metallic state, and this rate of reduction depends upon the specific mercury salt used and the acidity and temperature of the solution in which it is dissolved. It seemed desirable to determine which type of mercury salt solution can best be used in this process and to investigate the mechanism of the reactions involved as the exact nature of the changes taking place is not as yet known. A study was accordingly made of the rate and duration of the reaction of acetylene using various mercury salts in solutions of the corresponding acids at different concentrations and temperatures. Mercuric sulfate in dil. sulfuric acid solution was found to be most suitable for this purpose on account of the cheapness, activity, and lasting qualities of this catalytic solution. It was found, however, that in these solutions the mercury did not long remain in the form of the sulfate but was converted to an organic compound, and this compound acted as the catalyst.

Some reduction of mercury compounds to metallic mercury took place

in the dil. sulfuric acid solutions, and there was also a tendency for the acetaldehyde to form undesirable condensation products. With higher concentrations of sulfuric acid there was a decrease in the reduction of the mercury catalyst but an increase in the quantity of acetaldehyde destroyed. In attempting to avoid this dilemma a process was devised in which acid sulfate solutions of high concentration were substituted for dil. sulfuric acid, resulting in the production of fairly pure paraldehyde with very little mercury reduction. Since paraldehyde can readily be converted into acetaldehyde and can also be substituted for it in many reactions, it is thought that this process may be of commercial value. A process was also devised for the utilization of the acetaldehyde for the formation of quinaldine directly in a rather conc. sulfuric acid solution of the catalyst. There was slight mercury reduction and little loss of acetaldehyde by formation of condensation products. This indicates the possible advantage of using the acetaldehyde directly in the catalytic solutions for further synthesis.

A dry catalyst was also employed, consisting of a mixture of an organic mercury compound with an acid sulfate of ammonia or one of the alkali metals, and moist acetylene or a mixture of acetylene and steam was thereby slowly converted into acetaldehyde with no reduction of the mercury compound and no destruction of the aldehyde. From this and other indications it appears that the reduction of mercury salts in these processes is in some way due to their hydrolysis in aqueous solutions.

### Experimental.

#### I. Investigation of the Use of Different Mercury Salts as Catalysts.

Instead of passing a continuous stream of acetylene through the catalytic solutions and allowing the excess of gas to escape as has commonly been done, in all of these experiments the solutions were placed in a closed absorption vessel from which all air had been displaced by acetylene and this vessel was connected through a wash bottle with a gasometer filled with acetylene. The gas was rapidly absorbed on shaking the catalytic solution, and the rate, amount, and duration of absorption could be accurately ascertained by noting the reading of the gasometer and the flow of gas through the wash bottle, and by taring the absorption vessel.

It was soon found that many mercury salts in both acid and neutral solutions when shaken with acetylene would absorb it rapidly for a short time with the formation of precipitates, but that none of the neutral solutions and only a few of the acid solutions would continue to absorb readily after the precipitation had ceased.

Thus on the one hand, mercuric chloride in dil. hydrochloric acid and mercuric bromide in dil. hydrobromic acid absorb acetylene slowly for a time and then cease entirely to do so; while in stronger acid solution or in



concentrated solutions of halide salts no reaction occurs. Mercuric acetate in acetic acid solution also failed to react with acetylene after precipitation was complete, and mercuric phosphate in phosphoric acid solutions only absorbed acetylene very slowly after the initial reaction was over. *It is characteristic that the acetylene compounds of all of these salts were found to be only slightly soluble in the corresponding acids.*

On the other hand, mercuric perchlorate in perchloric acid, mercuric fluoborate in fluoboric acid, and mercuric nitrate in nitric acid, several of the mercuric sulfonates of the aromatic series in the sulfonic acids, and mercuric sulfate in sulfuric acid continued to absorb acetylene for a long time. *The acetylene compounds of all of these salts were found to be markedly soluble in the corresponding acids.* No acetaldehyde could be obtained from the nitric acid solutions, and the perchlorate, fluoborate, and sulfonates were considered too expensive for commercial use.

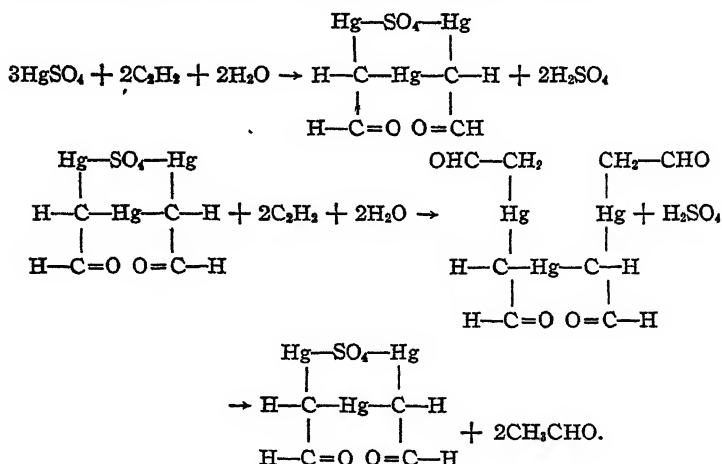
In view of these results the action of mercuric sulfate was submitted to a closer examination. It was found that in sulfuric acid of less than 20% concentration the catalyst is always reduced to metallic mercury with objectionable rapidity, on reaction with acetylene. The ratio of acetaldehyde formed to mercury salt reduced is accordingly very narrow in such a solution. With a sulfuric acid in concentrations above 20% the acetaldehyde cannot be distilled at ordinary pressure without the formation of large quantities of crotonaldehyde and tarry by-products, and the methods that have been devised for separating the acetaldehyde with organic solvents or of volatilizing it with excess acetylene or under reduced pressure are complex and expensive. We have accordingly studied the cause of these difficulties and have originated new processes in which they are at least partially obviated.

## II. The Nature of the Catalyst Compounds and the Cause of their Reduction to Metallic Mercury.

Exact information concerning the nature of the catalyst mercury compounds is very difficult to obtain by analytical methods on account of the high molecular weight of mercury, the inaccuracy of mercury determination, the constantly changing state of the catalyst, and the probability of the presence of numerous impurities in it. It has been frequently supposed that the inorganic salts of mercury acted as carriers of acetylene, but if this were the case some of the inorganic salt would be continually regenerated, especially if the supply of acetylene were shut off. However, no yellow mercuric oxide can ever be isolated from these mixtures by the addition of alkaline hydroxides; only white or gray organic substances are obtained in this way. It was not possible to detect any inorganic salts of mercury in any of the catalytic mixtures after the absorption of acetylene. The catalyst prepared from mercuric sulfate, moreover, always contained the

sulfate radical and at least one attached acetylene residue. The empirical formula,  $3\text{HgO} \cdot 2\text{C}_2\text{H}_2$ , has been fairly well established for the precipitate obtained by treating mercuric acetate in dil. acetic acid with acetylene.<sup>1</sup> When this compound is dissolved in dil. sulfuric acid it behaves in every way exactly like the compound precipitated from mercuric sulfate solutions with acetylene. It is therefore assumed that the precipitate from mercuric sulfate solutions is the sulfate of the same radical of which the precipitate from mercuric acetate is the oxide; and what appears to be a possible structural formula for this catalytic compound is given below. It is slightly soluble in strong alkaline solutions, and can be precipitated from such solutions with additional acetylene. Sulfuric acid releases a small quantity of acetaldehyde from this precipitate thus showing in two distinct stages the probable action in acid solutions. Small crystals of this catalyst can be obtained by dissolving it in warm dil. sulfuric acid and then cooling the solution.

The following reactions illustrate this point of view.



As far as is known, some acid is always liberated by the action of acetylene on the salts of mercury. It will be noted in the above reaction that the mercuric sulfate appears to supply all of the acid that is necessary, but nevertheless acid is always added to catalytic solutions in actual practice. An attempt was made to form acetaldehyde by passing moist acetylene over various mercury salts in the solid state. Mercuric chloride did not react with acetylene under these conditions. Nitrous fumes were liberated from mercuric nitrate by this method, but no acetaldehyde could be detected. From the reaction of mercuric sulfate with moist acetylene, acetaldehyde and free sulfuric acid resulted, and the acid immediately charred and polymerized a part of the aldehyde. When, however, moist

<sup>1</sup> Plimpton, *Chem. News*, 65, 295 (1892).

acetylene at  $100^{\circ}$  was passed over a dry finely divided mixture of sodium sulfate and mercuric sulfate, the sulfuric acid which was liberated combined with the sodium sulfate to produce sodium hydrogen sulfate, there was no charring, and a considerable quantity of pure acetaldehyde was produced. It was thus demonstrated that, under these conditions, mercuric sulfate will furnish all of the acid necessary for carrying on the reaction according to theory.

As a side reaction in all of these catalytic processes we are likely to have the continual reduction of mercury compounds to the metallic state, and this is a very serious commercial disadvantage. Numerous attempts have been made to prevent the reduction of mercury salts by the use of oxidizing agents in the solution. It is understood that none of these has proved of any value in practice. The salts of iron, manganese and vanadium were tried without securing any favorable results.

In general it was found that the greater the dilution of an acid solution the more rapidly mercury salts were reduced in it by the action of acetylene; and it is to be noted that the dilution of the acid is also closely related to the hydrolysis of mercury salts. The solutions of those mercury salts which hydrolyze most readily in their corresponding acids are also those in which the most rapid reduction takes place. Thus in dil. hydrochloric acid there is little reduction; in dil. sulfuric, somewhat more; in dil. nitric or acetic, a great deal. This leads us to the conclusion that, perhaps, most of the reduction of mercury salts is due to the action of acetylene or acetaldehyde on hydrolyzed mercury compounds, containing an oxide or hydroxyl group instead of an acid radical. Moist mercuric oxide is reduced by acetylene more rapidly than any other mercury compound. We find that this theory is also supported by the fact that in alcoholic solutions both hydrolysis and reduction are less than in aqueous solutions. It should be remembered that the catalytic mercury compounds, being organic, will probably hydrolyze much more in concentrated acid solutions than the corresponding inorganic salts.

On the other hand, we find some mercuric catalytic compounds reduced in conc. sulfuric acid where there is little possibility of hydrolysis. Charring of the organic matter always takes place in such solutions with the formation of sulfur dioxide. This substance will reduce mercury salts even in strong acid solutions, and the reduction in conc. sulfuric acid is thus accounted for.

The only way in which acetaldehyde could be obtained without the reduction of any mercury salt whatever was by the action of a stream of moist acetylene at  $70^{\circ}$  to  $120^{\circ}$  on a dry mixture of the mercuric sulfate acetylene compound and sodium, potassium, or ammonium hydrogen sulfates. This mixture could be made either by the action of moist acetylene on mercuric sulfate and the normal sulfates of sodium, potassium

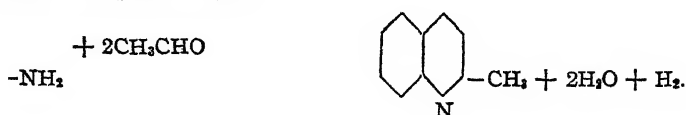
or ammonium finely ground together, as explained above; or the acid salt could be added to the washed and dried precipitate obtained from an acid mercuric sulfate solution by the action of acetylene. From such a mixture only about one gram of acetaldehyde per gram of mercury could be obtained in 12 hours, but there was no reduction of the mercury compound and the mass was perfectly soluble in water after use. When an excess of moisture or steam was used with the acetylene, a little of the mercury compound was volatilized. While this method may not be of much practical value, it serves to confirm the belief that the reduction of mercury compounds by acetylene is in some way due to their hydrolysis in dilute acid solution and points to the advantage of using stronger acid whenever possible.

It can also be shown that metallic mercury is slowly dissolved by the more concentrated solutions of sulfuric acid and the acid sulfates, but with acid strengths below 15% which have frequently been used for this purpose, this action is almost negligible.

The advantages of stronger acidity of the catalytic solutions having thus been demonstrated it became necessary to devise either a method for separating aldehyde from such strong acid solutions without the formation of undesirable by-products, or a method of utilizing the aldehyde directly in the solution for further synthesis and in this way avoiding the difficulties of separation.

### III. The Preparation of Quinaldine.

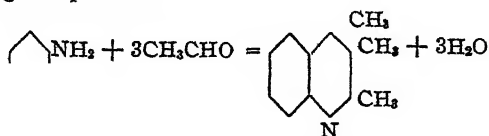
The acetaldehyde in these catalytic solutions was successfully substituted for pure acetaldehyde in the preparation of quinaldine. According to a standard process quinaldine is manufactured by treating aniline in hydrochloric acid or sometimes in sulfuric acid solution with a large excess of acetaldehyde or paraldehyde.



In the following process cheap acetylene takes the place of acetaldehyde. More concentrated sulfuric acid than can be used in making acetaldehyde from acetylene can be employed without the formation of tarry by-products. The violence of the standard quinaldine reaction is also avoided, giving more suitable conditions for manufacture on a large scale. In the old method a considerable excess of acetaldehyde was necessary, and in the new also it was found best to use an excess of acetylene. This can readily be done, since a given volume of the catalytic solution will absorb so much acetylene that the addition of a proportionate amount of aniline makes the mixture too viscous to handle.

Since quantities of a substance corresponding in properties to the

trimethyl-quinoline below indicated have been obtained in the process to be described, it is probable that under the conditions the following reaction takes place to a considerable extent in addition to the one which occurs in the regular process.



The following example will make clear the procedure.

Two g. of mercuric sulfate and 400 g. of aniline sulfate were dissolved in one liter of 40% sulfuric acid at 60° in a 2-liter flask which was then filled with acetylene, stoppered, and connected by a tube to a supply of acetylene under slight pressure. At this temperature fairly rapid absorption of the gas began at once but the speed was greatly accelerated by shaking the flask at frequent intervals. In a later experiment the same result was attained by using a drip absorption tower. In about 6 hours when 200 g. of acetylene had been absorbed, sodium carbonate was added until the solution was only slightly acid to litmus. The solution was then filtered and the precipitate contained practically all of the by-products, among them the substance thought to be trimethyl-quinoline above referred to. The filtrate was then made strongly alkaline with sodium hydroxide, causing the quinaldine and a small excess of aniline to separate as an oil. The quinaldine was purified by the ordinary methods and gave a yield of 80 g., which compares well with ordinary yields from the present commercial process.

Fifty g. of the dried by-product precipitate was heated for 5 hours at 200° with 50 g. of phthalic anhydride and 50 g. of zinc chloride, and the mass was then dissolved in hot conc. sulfuric acid and diluted in a process similar to the process for making quinophthalone from quinaldine. Considerable quantities of an orange dye were obtained showing that the original by-products were probably substituted quinaldines. The dye has properties very similar to quinophthalone, but produces an orange instead of a yellow color. The yield from the crude precipitate was only half of that calculated for trimethyl-quinoline of the same weight, on the basis that the phthalone was formed in the usual manner.

The concentration of the sulfuric acid used in these experiments varied from 10% to 95%. The temperature varied from 20° to 100°. A concentration of about 40% of sulfuric acid and a temperature of 60° seemed most advantageous. The use of phenol sulfonic and toluene sulfonic acids gave the same results as sulfuric acid. Aniline dissolved in 35% perchloric acid containing mercuric perchlorate gave very little quinaldine with acetylene and a large amount of the supposed trimethyl-quinoline. This substance separated from the acid solution and could be removed without neutralization.

The precipitate formed by the acetylene from mercuric acetate solutions was frequently used as a catalyst instead of the mercuric sulfate compound, and gave very satisfactory results.

It was found that the addition of acetone to the solution hastened the reaction, probably by increasing the solubility of the acetylene.

The aniline sulfate may be added at the beginning of the process, or while the absorption is going on, or aniline may be added when the absorption is complete, thus

neutralizing part of the sulfuric acid. It was found best to add at least part of the aniline as sulfate at the start as this tended to prevent the polymerization of acetaldehyde to tarry by-products.

It has been found possible to recover a portion of the excess acetaldehyde formed from the excess acetylene by diluting the sulfuric acid to a concentration of less than 10% and distilling the aldehyde.

The action of substituted anilines is exactly analogous; the toluidines, for example, yield the corresponding methyl-quinolines.

It will be noted that according to theory no water is used in this reaction, and this led to an attempt to carry on the process by using aniline sulfate, sodium hydrogen sulfate, mercuric sulfate, and acetylene in a nearly dry state. Acetylene was absorbed rapidly at first and some quinaldine was formed, but the mass soon became a viscous semi-solid into which the acetylene could not penetrate.

It was also found that the preparation of quinaldine could be carried on in absolute alcohol solution with dry acetylene. This points to the possibility that acetaldehyde may not be an intermediate product, but that the aniline may react directly with the mercury acetylene compound.

The preparation of aldehyde green is a related reaction that can also be performed with acetylene instead of acetaldehyde or paraldehyde. A present standard method for the synthesis of the commercial product is to treat fuchsin in rather strong sulfuric acid with about  $\frac{1}{3}$  of its weight of paraldehyde, then boil with sodium thiosulfate, filter, and treat the filtrate with sodium acetate. In this experiment 40 g. of fuchsin was dissolved in 100 g. of 50% sulfuric acid, containing 1 g. of mercuric sulfate, and the solution was allowed to absorb 7 g. of acetylene. It was then boiled with 5 g. of sodium thiosulfate, filtered, and treated with 8 g. of sodium acetate. Both a green and a blue dye were present. The mixture did not absorb acetylene very readily, but this may have been due to the presence of chloride in the fuchsin.

#### IV. Preparation of Paraldehyde.

It was often noted that when solutions containing acetaldehyde were allowed to stand for a few days an odor of paraldehyde developed, and in a few cases droplets of paraldehyde separated from perchloric and sulfuric acid solutions. It was next found that a mixture of sodium hydrogen sulfate and mercuric sulfate in a moist state became covered with a film of paraldehyde when acted upon by acetylene and this action is the basis of the process to be discussed.

The most convenient apparatus for carrying on this reaction in the laboratory is a large bottle or carboy filled with fragments of glass or porcelain. These are covered with a pasty mass made up of an acid salt, a catalytic mercury compound, and a small amount of saturated aqueous solution of the acid salt. The air in the apparatus is then displaced by acetylene, the carboy tightly stoppered, and acetylene led into the apparatus as fast as it is used. The carboy is rolled occasionally to keep the catalytic mixture evenly distributed

Mercuric sulfate, mercuric acetate, the acetylene compounds of the two salts precipitated from acid solution, and mercuric oxide were used in different experiments without markedly different results. Mercuric phosphate was not so good.

Acid phosphates and sulfates of ammonium, sodium, and potassium were experimented with. The acid phosphates were discarded because of their slow action and high mercury reduction. Sodium hydrogen sulfate is the cheapest material and is perfectly satisfactory for this purpose. Ammonium hydrogen sulfate solutions dissolved more acetylene and more of the resulting paraldehyde than any of the others.

The solution of acid salt must be saturated because reduction of mercury takes place more readily in dilute solutions, and it is best to have an excess of undissolved acid salt in the apparatus in order to saturate rapidly any water that may be added from time to time. As little solution as possible was used in most of these experiments, because larger amounts dissolved the paraldehyde and retarded its separation. Since the saturated solutions of the acid sulfates do not dissolve either acetylene or the mercury acetylene catalytic compound to a very great extent, it is necessary to have the acetylene come in direct contact with the solid catalyst, and this is prevented by the presence of much solution.

In this process acetaldehyde is first formed by the action of the mercury acetylene compounds on acetylene and water. The acid salts at ordinary temperatures and in saturated water solutions or in solid form, then rapidly and completely polymerize the acetaldehyde to paraldehyde. As paraldehyde is but slightly soluble in saturated solutions of the acid salts, it separates as a distinct layer and may be drained off in a fairly pure condition. The paraldehyde shows little tendency to cling to the catalyst mixture as long as this is protected by a film of moisture, and no solid matter is ever suspended in the paraldehyde.

The absorption of acetylene is more rapid after a certain amount of paraldehyde has been formed in the apparatus. The reason is that the paraldehyde dissolves the unconverted acetaldehyde vapor which would dilute the acetylene and thus slow up absorption and also because paraldehyde dissolves acetylene and brings it into more immediate contact with the catalysts.

The water needed in the reaction can be partially supplied by using moist acetylene, but more water must be added as often as the amount in the apparatus diminishes. It is better to add the water in small amounts and with thorough mixing, as a sudden dilution causes a sudden and notable graying and reduction of the mercury.

Considerable amount of certain impurities, especially the halides retard the absorption of acetylene greatly. Free sulfuric acid hastens absorption but the resulting paraldehyde is dark in color and contains

traces of crotonaldehyde. It should be noted that when mercuric sulfate reacts with acetylene sulfuric acid is liberated, and this will produce the same effect in a mixture as added sulfuric acid. When mercury is introduced in the form of sulfate it is best to add a small amount of the normal salt corresponding to the acid salt used to take up any free sulfuric acid that may be formed in this way. When this precaution is observed the paraldehyde is clear and colorless, and the excess of normal salt does not materially affect absorption.

The following example of laboratory procedure will serve to illustrate the process.

A 2-liter bottle was filled with clean dry glass fragments, and a mixture of 10 g. of mercuric sulfate, 40 g. of sodium hydrogen sulfate and 20 g. of water was then distributed over the surface of this packing material. The air was displaced by acetylene and the bottle tightly closed except for the inlet tube through which moist acetylene under slight pressure was continuously supplied from a gasometer. As soon as the white compound of acetylene and mercuric sulfate had been formed, acetaldehyde could be detected in the apparatus, and shortly afterward paraldehyde was also shown to be present. When about 25 g. of acetylene had been absorbed, paraldehyde began to accumulate in visible drops. Thereafter the formation of paraldehyde was practically quantitative. The production from the apparatus used was about 60 g. per day, and the total amount obtained was 287 g.

In another experiment a mixture of 295 g. of sodium hydrogen sulfate, 250 g. of water, and 75 g. of mercuric nitrate was used in the same way. Ten cc. of nitric acid was added at the end of both the fifth and ninth day, and this seemed to redissolve some of the reduced mercury and increase absorption slightly. Water was added in small quantities as needed. The paraldehyde was drained off daily, and at the end of the tenth day when the experiment was accidentally lost, the total amount obtained was 1100 g.

A mixture of 1250 g. of ammonium hydrogen sulfate, 200 g. of water, and 300 g. of mercuric nitrate was allowed to absorb acetylene for a few days before the separation of paraldehyde began. It then yielded from 300 to 500 g. of paraldehyde per day, with some interruptions due to lack of acetylene, and at the time of this writing is still running and has given a total yield of 3400 g. of paraldehyde, an aldehyde-mercury ratio of 17:1.

A mixture containing 200 g. of potassium hydrogen sulfate, and 50 g. of mercuric sulfate with frequent small additions of water absorbed acetylene for 130 days. Twenty-five g. of mercuric sulfate was then added and the experiment was carried on for 35 days longer. A total yield of 1800 g. of paraldehyde was obtained, giving an aldehyde-mercury ratio of 35:1.

The paraldehyde prepared by this method contains a small amount of dissolved water and acid salt, and, if the separation takes place immediately after absorption, unchanged acetylene and acetaldehyde may be present. These impurities were never found to run higher than 5%. The heat of formation of the paraldehyde did not appear to be as great as was expected. A 20-liter carboy of the mixture distributed over glass fragments absorbed acetylene at the rate of 2 liters per minute.

### Summary.

It was shown by experiments on the relative value of different mercury salts as catalysts for the conversion of acetylene to acetaldehyde that



mercuric sulfate in sulfuric acid solution is the cheapest and most efficient for the purpose. It was found that the chief difficulties in its use lie in the impossibility of separating acetaldehyde from the more concentrated acid solution and in the rapid reduction of the mercury compounds in the dilute acid which is now commercially employed. The reduction of mercury compounds by acetylene and aldehyde is greatest where the conditions are the most favorable for hydrolysis, and the catalytic mercury compounds being organic are probably more readily hydrolyzed than the inorganic salts of mercury. No reduction takes place in a suitable dry mixture where there is no hydrolysis but this method is too slow for commercial use. Attention was therefore turned to methods of utilizing acetaldehyde in rather concentrated solutions of sulfuric acid or the acid sulfates.

A new method for the synthesis of quinaldine and related products has been worked out. A new paraldehyde process has been developed which is capable of being used as a substitute for the method of acetaldehyde production now in use and which has the following advantages: (1) the ratio of aldehyde to reduced mercury is much higher; (2) the apparatus is simpler and the catalyst less bulky; (3) no distillation or separation process is necessary; (4) there are no by-products and no waste products; (5) there is no excess acetylene to be recovered.

NOTRE DAME, INDIANA.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE EXISTENCE AND REACTIONS OF POSITIVE HALOGEN ATTACHED TO CARBON IN AROMATIC COMPOUNDS.

BY BEN H. NICOLET.

Received May 4, 1921.

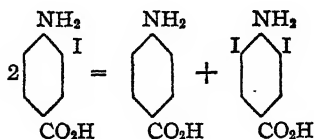
The halogen atoms in certain organic compounds have the property of being replaced by hydrogen, and appearing combined with the hydroxyl group as hypohalous acids, on hydrolysis. This behavior is frequently expressed by referring to such atoms as positive halogen atoms. Most, if not all, of the compounds in which halogen replaces the hydrogen of an hydroxyl, amino, or imino group, have this halogen in the positive form.

Without doubt, halogen attached to carbon is usually negative. Nevertheless, Howell and Noyes<sup>1</sup> have recently offered excellent evidence that iodine is positive in the compound  $C_2I_2$ . Fry<sup>2</sup> had previously assigned a structure involving positive chlorine and bromine, to certain aromatic compounds, but primarily on the ground of the extreme difficulty of hydrolyzing such compounds. The negative test of non-reaction is necessarily an uncertain basis for the assignment of electronic structures.

<sup>1</sup> Howell and Noyes, *THIS JOURNAL*, **42**, 991 (1920).

<sup>2</sup> Fry, *ibid.*, **38**, 1327, 1333 (1916).

It is the object of the present paper to call attention to certain aromatic halogen compounds whose reactions are such as would be expected if the halogens were in the positive form. Typical of all these cases so far examined, is the reaction observed by Wheeler and Liddle,<sup>3</sup> which takes place when 3-iodo-4-aminobenzoic acid is boiled for a "few minutes" with hydrochloric acid.



Obviously, iodine is here removed in such a manner as to be replaced by hydrogen; and yet the first stage of the reaction can scarcely involve a reduction, since the iodine thus removed is capable of resubstitution in the benzene ring. The latter reaction is only given by positive iodine. The formation of the di-iodo derivative is thus fairly good evidence of the intermediate formation of some product such as represented by the formulas HOI or CII, and confirms the positive nature of the original halogen.

Similar reactions have been observed by Limpricht<sup>4</sup> on several amino-bromo-benzene sulfonic acids, and by Fittig<sup>5</sup> on *p*-bromo-aniline. In both cases, however, temperatures of 150° or higher were necessary.

It has now been found that 3-iodo-4-aminotoluene, 4-iodo-aniline, 3-bromo-4-acetamino-toluene, and 3-iodo-4-hydroxybenzoic acid, when boiled with 10% hydrochloric acid, are hydrolyzed with a readiness decreasing in the order named, in such a way that the halogen is removed and replaced by hydrogen; and further that the halogen is in each case re-substituted in the benzene ring to give di-(or tri-) halogen substitution products. This is considered to be the best evidence yet offered for the existence of "positive" halogen attached to carbon in the benzene nucleus. It will be noticed that in all the cases mentioned the halogen in question is *ortho* or *para* to a strongly negative group.

It has also been found that alkali is incomparably less effective than acid in removing such "positive" halogens, as was to be anticipated. This is true even when sodium arsenite is added to the alkaline solution; but this is not particularly surprising, since in acid solution also, the product of hydrolysis, HOX, is effectively removed, either by resubstitution or by conversion to HX and HXO<sub>3</sub>.

In the presence of stannous chloride, naturally, the same hydrolysis takes place; but here resubstitution is prevented, and the halogen is simply removed from the molecule. This reaction, involving as it does the

<sup>3</sup> Wheeler and Liddle, *Am. Chem. J.*, **42**, 453-7 (1909).

<sup>4</sup> Limpricht, *Ber.*, **10**, 1541 (1877).

<sup>5</sup> Fittig, *Ann.*, **188**, 20, 24, 28 (1877).

use of a reducing agent, is valueless for the proof of electronic structure, but in the few cases investigated it runs so definitely parallel to the action of acid alone, that it may yet prove valuable as a preliminary test for positive halogens in aromatic compounds.

The present paper is purely preliminary, and further work is contemplated on all the questions raised, particularly as regards aromatic derivatives.

### Experimental Part.

**3-Iodo-4-aminotoluene.**—The base was prepared according to Wheeler and Liddle.\* Boiled with 10% hydrochloric acid, the color of iodine vapor was visible almost at once and at the end of 10 minutes, di-iodo-toluidine could be isolated. An hour's boiling was sufficient (perhaps more than sufficient) to give complete conversion to toluidine and 3,5-di-iodo-toluidine, both of which were identified.

**3-Bromo-4-acetamino-toluene.**—On boiling for an hour with 10% hydrochloric acid, noticeable amounts of 3,5-dibromo-toluidine had sublimed into the condenser. The reaction is however much slower than that of the iodine compound, as even after boiling for 5 hours, only 6-7% of the theoretical amount of the dibromo-derivative had been formed, and on re-acetylation, most of the original material was recovered unaltered. Toluidine was identified only by the color reaction with sodium hypochlorite.

**4-Iodo-aniline.**—Boiling with 10% hydrochloric acid seemed to cause liberation of iodine readily (as judged by the color), but after an hour the transformation was far from complete. The solution contained aniline, and a mixture of iodoanilines.

**3-Iodo-4-hydroxybenzoic Acid.**—After an hour's boiling, an appreciable amount of the di-iodo acid had separated from the originally clear solution. At the end of 6 hours, the yield of 3,5-di-iodo-4-hydroxybenzoic acid was only 6.7% of that theoretically possible, and much unaltered product was isolated.

**Action of Alkalies.**—Mono-iodo-toluidine was recovered quantitatively unaltered after heating for 3 hours with an excess of alkaline sodium arsenite solution in dil. alcohol. The solution gave no test for iodide. Refluxing for 3 hours with 10% alcoholic potash was also without effect, and did not produce an odor of isocyanide. (Alcohol reacts much more readily than do aromatic amines, with alkaline hypo-iodites; when iodine is added to an alkaline alcoholic solution of aniline, for instance, the isocyanide odor appears promptly and unmistakably.)

**Action of Mild Reducing Agents in Acid Solution;  $\text{SnCl}_2$ .**—The various substances were boiled under reflux with 10% hydrochloric acid containing an excess (2 mols.) of stannous chloride.

**4-Bromo-aniline**, after one hour, scarcely gave a color test for aniline. After 5 hours the test was very distinct; but at the end of 8 hours most of the original bromo-aniline was recovered unchanged.

**3-Iodo-4-aminotoluene**, heated for one hour, gave practically pure *p*-toluidine, m. p.  $42^\circ$ , which liquified on mixing with the original base.

**3,5-Di-iodo-4-aminotoluene**, after 8 hours, had gone into solution almost completely. Steam distillation of the alkaline solution gave *p*-toluidine, recognized by its color reaction with hypochlorite, and by its acetyl derivative, m. p.  $152^\circ$ .

**4-Iodo-aniline**, heated for one hour, gave tests for aniline and for iodide. After 4 hours, the reaction was somewhere near complete, as steam distillation gave a liquid base, whose crude acetyl derivative, melted at  $113^\circ$ .

**3-Bromo-4-acetamino-toluene** gave qualitative indications of reaction after one hour. After 8 hours, debromination was slightly more than 75% complete.

3-Iodo-4-hydroxybenzoic acid, after one hour, showed little sign of reaction. After 5 hours, the solution contained considerable iodide, but the reaction was very incomplete.

Iodobenzene, treated as above and boiled for 5 hours, showed no evidence whatever of reaction. The same result was obtained when alcohol was added to render the substance more soluble. In both cases the test for iodides was negative.

### Summary.

1. It has been shown that certain compounds containing iodine or bromine *ortho* or *para* to an amino or anhydroxyl group, when boiled with hydrochloric acid in part replace their halogen by hydrogen and in part give di- (or tri-) substitution products. Together, these reactions are considered to characterize these derivatives as containing positive halogen.

2. In similar compounds, iodine is more positive than bromine, and *ortho* than *para* compounds.

3. Compounds which, by the above standards, contain positive halogen, are abnormally readily dehalogenated by stannous chloride, in acid solution.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## NITROMALIC ACID.

By ARTHUR LACHMAN.

Received May 12, 1921.

The abnormal action of alkalis upon organic nitrates, whereby varying and at times considerable amounts of nitrous acid are produced, has been accounted for in two quite different manners. Nef<sup>1</sup> assumed what he called "methylene dissociation" to take place, and definitely ascribed this dissociation to the alkali. Klason and Carlson,<sup>2</sup> holding the view that nitric acid is a peroxide, looked upon the formation of nitrous acid as a direct hydrolysis of the nitric ester into nitrous acid and an organic peroxide. They also regarded the alkaline reagent as an essential factor.

The recently noted behavior of nitrotartaric acid,<sup>3</sup> hydrolyzing normally and almost quantitatively as a true nitric ester in strongly acid media, and equally quantitatively as a nitrous ester in weaker acid, did not accord with either of the above interpretations. The suggestion was made that nitrotartaric acid goes over into a pseudo form,  $\text{COOH.CH(ONO}_2\text{).CH(ONO}_2\text{).COOH} \rightarrow \text{COOH.C(OH)(ONO).C(OH)(ONO).COOH}$ . Nitrotartaric acid, being soluble both in water and organic solvents, seemed to offer a better opportunity for the investigation of what really happens in these intramolecular oxidations, than the esters studied by Nef and by Klason and Carlson. At the same time, Michael's view that

<sup>1</sup> Nef, *Ann.*, 309, 176 (1899).

<sup>2</sup> Klason and Carlson, *Ber.*, 40, 4183 (1907).

<sup>3</sup> Lachman, *THIS JOURNAL*, 43, 577 (1921).

the *solvent* frequently determines the course of a reaction, could be considered.

It proved difficult, however, to keep nitrotartaric acid under sufficient control for purposes of measurement. The search for a more suitable compound was fortunately of brief duration. Nitromalic acid, the nitrate of ordinary malic acid, soon gave promising results. This acid, which has not yet been described, is easily prepared.

### Preparation and Properties of Nitromalic Acid.

Dissolve 10 g. of malic acid in 20 cc. of nitric acid (1.42), warming slightly if necessary. Add this solution, with careful cooling and stirring, to 40 cc. of fuming sulfuric acid (10–15%). Pack this material in ice, and allow it to stand for 2 hours. Pour the product upon cracked ice, extract the liquid twice with ether, wash the ether and extract it thrice with small quantities of ice water to remove the excess of nitric acid. Dry this solution thoroughly with calcium chloride. Careful evaporation of the ether gives a thick white oil, which soon solidifies to form a stellated mass of long, soft, white needles. Yield, 6 to 7 g.<sup>4</sup>

Nitromalic acid as thus obtained is sufficiently pure for analysis; a portion, however, was recrystallized from dry ether by addition of ligroin. It melts, with decomposition, at 110–112°. It is very soluble in water, alcohol, ether, and acetone, and is insoluble in ligroin and benzene. The composition is  $C_4H_5NO_7$  corresponding to the structure  $COOH.CH_2-CH(ONO_2).COOH$ ; mol. wt., 179.1.

Subs., 1.0054: 22.45 cc. of 0.5 N NaOH.<sup>5</sup> Calc.: 22.47 cc.

Subs., 0.5044: (boiled with excess of diluted 0.5 N NaOH, cooled and titrated) 17.15 cc. Calc.: 17.05 cc. for 1.5 moles.

The *sodium* salt of nitromalic acid was prepared by carefully neutralizing the acid with sodium carbonate, and evaporating the solution at room temperature over sulfuric acid. It forms small hard white crystals, is very soluble, but not deliquescent. It holds two molecules of water. The dry sodium salt explodes when heated.

*Analysis.* Subs., 0.0897:  $Na_2SO_4$ , 0.0500. Calc. for  $Na_2C_4H_5NO_7 \cdot 2H_2O$ : Na, 17.75. Found: 18.25.

The *silver* salt was prepared by addition of silver nitrate to a solution of the sodium salt. It forms small white crystals, and is moderately soluble in water. It is anhydrous. On heating, it explodes. For analysis, it was moistened with ammonium sulfide, and then ignited.

*Analysis.* Subs., 0.2321: Ag, 0.1271. Calc. for  $Ag_2C_4H_5NO_7$ : Ag, 54.9. Found: 54.8.

<sup>4</sup> It is not desirable to prepare nitromalic acid in larger amounts. A lot made from 30 g. of malic acid, from which the ether was evaporating spontaneously, exploded during the night. A second preparation with similar quantities decomposed during the evaporation of the ether.

<sup>5</sup> Nitromalic acid is not strong enough to be titrated with methyl orange as an indicator. The above titrations were made at 0°, with phenolphthalein as an indicator. Combustion gave high results for C, because of formation of nitric oxide. Calc.: H, 2.79. Found: 2.85.

### Hydrolysis by Aqueous Alkali.

Nitromalic acid was treated with sodium hydroxide in water solution; both concentration of the acid and the excess of the alkali were varied within wide limits. The reaction was completed very rapidly; 5 minutes' heating on the water-bath sufficed. Temperature seems to have no effect on the production of nitrous acid; in two cases, the reaction mixture was allowed to stand in the cold for several days. The results obtained are given in the following table.

TABLE I.

#### HYDROLYSIS BY AQUEOUS ALKALI.

Nitromalic Acid, Weight. G.	Millimols.	NaOH, Millimols.	Volume. Cc.	NaNO <sub>2</sub> . %.
0.3056	1.7	10	70	21.0
0.5170	2.9	18	9	21.6
0.5009	2.8	55	9	21.0
0.1790	1.0	12	30	20.3
0.2720	1.5	30	10	20.6

The amount of nitrous acid formed is practically constant, regardless of temperature, concentration, or excess of alkali. This is in complete agreement with the data obtained by Klason and Carlson<sup>2</sup> who studied the hydrolysis of alkyl nitrates by alkalies in the presence of mercaptans.

The method of estimating the amount of nitrous acid produced in the above hydrolyses must be described briefly, as it subsequently led to interesting results. The small flasks containing the reaction mixture were connected to a carbon dioxide supply and when all the air had been swept out, to an azotometer. A solution of a slight excess of sulfanilic acid in dil. acetic acid was then added all at once through a dropping funnel. After allowing the diazo reaction about 5 minutes in which to complete itself, the material in the flask was slowly warmed to boiling; nitrogen is evolved so rapidly that the entire operation required about 20 minutes. Each mol. of nitrous acid gives one mol. of nitrogen.

### Hydrolysis by Alkali in Methyl Alcohol.

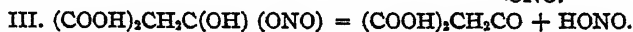
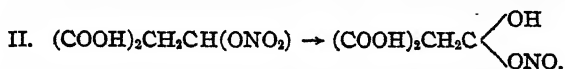
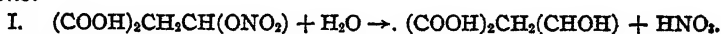
Upon the addition of sodium hydroxide, dissolved in methyl alcohol, to a solution of nitromalic acid in the same solvent, a portion of the sodium nitromalate first formed by neutralization, is precipitated. In spite of the lack of homogeneity in the system, the amount of nitrous acid formed is again practically independent of temperature, concentration, or excess of alkali; *but nearly twice as much is produced as when water is the solvent.*

TABLE II.  
HYDROLYSIS BY ALKALI IN METHYL ALCOHOL.

Weights G.	Nitromalic Acid. Millimols.	NaOH. Millimols.	Volume. Cc.	NaNO <sub>2</sub> . %.
0.5353	3.0	9.2	5	32.6
0.5001	2.8	18	9	39.9
0.5163	2.9	50	20	34.4
0.3775	2.1	17	15	35.5
0.3163	1.8	10	23	34.6
0.2383	1.3	30	30	35.6

### Hydrolysis in Acid Solution.

The preceding data pointed to the conclusion that the solvent is the determining factor in the abnormal hydrolysis of nitrates; but on further consideration it became clear that what was measured above was not the formation of nitrous acid, *but the competition between two or three different reactions.*



Reaction I represents the normal hydrolysis of nitromalic acid into its components. Reaction II is the process of isomerization according to the present conception; it might represent equally well, with a slight change in formulation, what Nef called "methylene dissociation," or Klason's "peroxide formation." Reaction III is the simple hydrolysis of the nitrous ester.

Klason and Carlson have found that the normal saponification of a nitrate takes a measurable time, while the hydrolysis of nitrites is practically instantaneous. The data obtained above, then, represent the ratios of the velocities of Reactions I and II; and any influence that can be exerted upon Reaction I to slow it down, will inevitably increase the proportion in which Reaction II takes place.

This makes clear the influence of methyl alcohol upon the amount of nitrous acid produced; Reaction I requires water for its mechanism, and as the amount of water present is very small, it must be greatly retarded. Consequently, more time is available for the structural change, and more nitrous acid is found.

It is further clear that if Reaction I could be retarded still further, even more nitrous acid might be expected. With this purpose in mind, alkali was excluded altogether, and nitromalic acid warmed directly with aqueous sulfanilic acid.

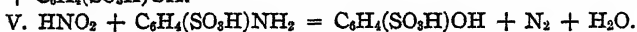
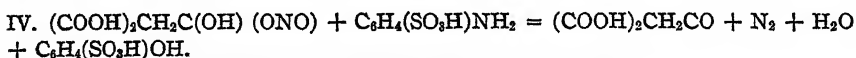
Nitrogen was found to be given off slowly, and at a rapidly diminishing rate. The first experiment was maintained for 2 hours at water-bath

temperature, and gave 65% nitrogen. A second test, lasting 5 hours, gave 78.3%.

These striking figures at once eliminate the hypotheses of Nef and of Klason.

### Velocity of the Structural Change.

The very moderate rate at which nitrogen was evolved in the experiments just described, made it possible to measure the velocity of the process. Besides the reactions under (II) and (III), both of which are monomolecular, the following possibilities were to be considered.



Equation IV represents the possible direct interaction of nitromalic acid, either in the normal or the pseudo form, with sulfanilic acid. Equation V is the reaction upon which the method of measurement is based. Of these reactions, (II) and (III) are monomolecular; but (III) is very rapid in comparison to (II), and will therefore interfere to but a small extent. Reaction IV is bimolecular; (V) is also bimolecular, but very rapid.

The results obtained in two series of measurements are given in the following table. Nitromalic and sulfanilic acids were dissolved in cold water, and not placed in the boiling water-bath until all air had been expelled. Carbon dioxide was bubbled through the liquid at the rate of 3 bubbles per second. The gas was not entirely free from air; the amount of air accumulated per hour was determined, and the volume of nitrogen corrected accordingly. The temperature of the azotometer was constant within 1°. Time was recorded from the beginning of heating. This seemed better than making a perhaps dubious allowance for the initial lag. Towards the end of the reaction, the carbon dioxide was absorbed rather slowly making the volume readings uncertain; the later values are not included.

TABLE III.

#### REACTION BETWEEN NITROMALIC AND SULFANILIC ACIDS.

0.4172 G. of nitromalic acid + 0.7420 g. of sulfanilic acid; volume 45.0 cc. Bath at 100°. Gas measured at 21°—740 mm. (corr.). 1 cc. of N<sub>2</sub> equivalent to 0.000877 mols./liters transformed.

Min.	N <sub>2</sub> Cc.	<i>x</i> .	<i>a</i> — <i>x</i> .	<i>K</i> .	<i>b</i> — <i>x</i> .	<i>K'</i> .
0	..	....	0.0518	....	0.0788	....
5	2.5	0.0022	0.0496	0.0038	0.0766	0.0044
10	5.6	0.0049	0.0469	0.0043	0.0739	0.0055
15	8.0	0.0070	0.0448	0.0042	0.0718	0.0054
20	10.7	0.0094	0.0424	0.0043	0.0694	0.0057
25	13.4	0.0118	0.0400	0.0045	0.0670	0.0061
40	19.6	0.0172	0.0346	0.0044	0.0616	0.0063
55	24.5	0.0215	0.0303	0.0042	0.0573	0.0063
70	28.6	0.0251	0.0267	0.0041	0.0537	0.0064
85	32.0	0.0281	0.0237	0.0040	0.0507	0.0063

0.4031 G. of nitromalic acid + 0.4838 g. of sulfanilic acid. Volume 35.0 cc. Bath at 100°. Gas measured at 21°. 740 mm. 1 cc. of N<sub>2</sub> = 0.001132 mol./liters transformed.



TABLE III (continued).

Min.	Ns. Cc.	$x$ .	$a-x$ .	$K$ .	$b-x$ .	$K'$ .
0	..	....	0.0643	....	0.0661	....
6	2.2	0.0025	0.0618	0.0028	0.0636	0.0093
12	5.4	0.0061	0.0582	0.0036	0.0600	0.0600
20	9.9	0.0112	0.0531	0.0042	0.0549	0.0611
32	16.1	0.0182	0.0461	0.0045	0.0479	0.0764
40	19.1	0.0216	0.0427	0.0045	0.0445	0.0847
70	28.2	0.0319	0.0324	0.0043	0.0342	0.0945
90	33.9	0.0384	0.0259	0.0041	0.0277	0.1003
120	37.9	0.0429	0.0214	0.0040	0.0232	0.1095

In the table  $K$  is the value of the constant calculated for monomolecular reaction,  $K'$  for bimolecular. Considering the rather imperfect technique, there is good agreement for  $K$  in the two series, in spite of the considerable difference in concentration. The values of  $K'$  do not agree among themselves and in the second series they become absurd.

The conclusion is therefore justified that the reaction in question is monomolecular, and that Equation IV may be excluded from further consideration. Inasmuch as Reaction III is known to be a very rapid process, the value of  $K$  obtained above may be regarded as substantially indicating the velocity of the structural change.

The formation of oxalo-acetic acid, according to Equation III, was definitely established. From 1.0 g. of nitromalic acid, heated for several hours with a solution of sulfanilic acid, there was obtained by ether extraction 0.15 g. of crude product, melting at about  $120^{\circ}$ ; on recrystallizing from ether and ligroin, the melting point rose to  $180^{\circ}$ .

### Hydrolysis in Neutral Solution.

In order to ascertain the action of nitromalic acid in a solution as nearly neutral as possible, 1.0 g. of sodium nitromalate was dissolved in 100 cc. of water. To this solution, about 1.0 g. of calcium carbonate was added, and the mixture was boiled vigorously, with mechanical stirring, for 2 hours. The volume was maintained approximately constant.

The amount of nitrous acid formed was 8%. The residual solution, free from nitrous acid, gave a copious precipitate with nitron, showing the presence of nitric acid; and the filtrate from this, on evaporation, left a residue which was identified as calcium malate.

### Discussion of Results.

The very considerable variation in the amount of nitrous acid formed from nitromalic acid (from 8% to 80%) under varying experimental conditions, is a convincing illustration of the need of closely defining the working conditions, if a clear picture of the course of an organic reaction is to result. In far too many cases it has been the custom to seize upon the

product that happens to be formed more readily under one set of circumstances, and to regard that product as the main, or even the exclusive, result of the reaction.

In the present case, it would have been quite possible, merely by discontinuing the work, to reach two fallacious conclusions; (1) that the production of nitrous acid is due chiefly to the action of alkali; (2) that alcoholic alkali exerts a greater influence than aqueous.

The truth is that alkali merely catalyzes the formation of nitrous acid, *i. e.*, increases the rate at which it is produced. But at the same time, the alkali catalyzes the normal hydrolysis into *nitric* acid to a still greater extent; and the net result of employing alkali is to diminish the *amount* of nitrous acid, as compared with that formed in acid solution.

It is clear, then, that in the hydrolysis of nitric esters two processes are occurring side by side. Any factor which will hasten one, will make the other lag in comparison. What appears to be an equilibrium, as for instance in the case of hydrolysis by aqueous alkali, is merely a ratio of two rates of reaction. The real action of alcohol, which appears to increase the proportion of nitrous acid, is to slow down the normal hydrolysis into nitric acid.

There can be little doubt that many such false equilibria have served to cloud our understanding of organic reactions. This is conspicuously the case in the so-called molecular rearrangements. Molecular rearrangements resemble the behavior of nitrotartaric and nitromalic acids in that they also involve intramolecular oxidations and reductions. We are not justified in drawing conclusions in this complex field on the basis of a single product which may represent less than half the material originally taken, or even when the product is quantitatively defined but its mode of preparation not varied between sufficiently wide limits.

By the aid of this point of view, it has been possible to secure some interesting and unexpected results along well-worn trails. These will be reported in the near future.

The present studies were begun and completed in the laboratory of the University of California, which with unexampled and unlimited generosity has placed all its facilities at my disposal. It is difficult to express my indebtedness to and gratitude for the courtesies and encouragement extended by Professors G. N. Lewis and E. O'Neill and the entire staff.

### Summary.

1. The preparation and properties of nitromalic acid are described.
2. Nitromalic acid yields a mixture of nitric and nitrous acids when hydrolyzed with aqueous alkali. The percentage of nitrous acid is independent of temperature, concentration or excess of alkali.

3. Hydrolysis in alcoholic solution gives similar results; the percentage of nitrous acid is independent of experimental conditions, but nearly twice as much is formed as in the previous case.

4. The reason for this difference is discussed.

5. It was found that when alkali is excluded altogether, and a substance like sulfanilic acid added, which can take up nitrous acid as fast as formed, the production of nitrous acid is greatly increased.

6. The rate of formation of nitrous acid under the latter conditions was found to be monomolecular.

7. In the hydrolysis of nitric esters two processes occur independently of each other. One is the normal saponification into alcohol (or oxyacid) and nitric acid; the other is isomerization to a nitrous ester, which subsequently hydrolyzes into a carbonyl compound (aldehyde or ketone) and nitrous acid. Each of these reactions proceeds at its own rate under the given conditions.

8. The constant yield of nitrous acid obtained when, for example, aqueous alkali is employed is a false equilibrium. The real constant is the ratio of the rates of the two reactions.

BERKELEY, CALIFORNIA.

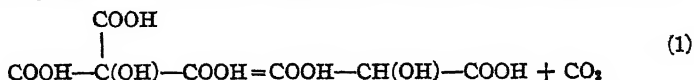
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## DIHYDROXY-TARTARIC ACID.

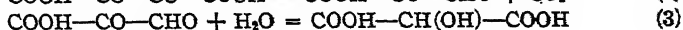
BY ARTHUR LACEMAN.

Received May 18, 1921.

Dihydroxy-tartaric acid was first obtained by Gruber,<sup>1</sup> by the action of nitrous acid on protocatechuic acid. He found that it readily lost carbon dioxide, with formation of tartronic acid; he therefore named the compound carboxy-tartronic acid, and ascribed to it the following structure.



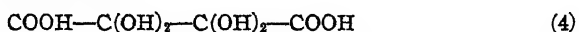
As the formation of an acid of this structure from the oxidation of a benzene ring appeared to support the prism rather than the hexagon formula, the subject was promptly investigated by Kekulé.<sup>2</sup> The latter obtained Gruber's acid from nitrotartaric acid, and was able to reconvert it into tartaric acid by reduction. He explained the formation of tartronic thus: first, loss of carbon dioxide and production of an aldehydo-acid, and second, rearrangement of the aldehydo-acid.



<sup>1</sup> Gruber, *Ber.*, 12, 514 (1879).

<sup>2</sup> Kekulé, *Ann.*, 221, 245 (1883).

Kekulé wrote these equations with the keto groups dehydrated, although as a matter of fact the free acid and its salts all hold at least two mols of water, and should be formulated



as a true dihydroxy-tartaric acid.

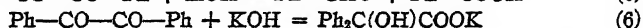
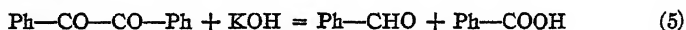
Nearly 20 years later, Fenton<sup>3</sup> prepared glyoxyl-formic acid of the formula shown in Equation 2, and found that it did indeed readily pass over into tartronic acid on warming with alkalis, according to Equation 3.

Kekulé's explanation, however, fails to account for the fact that the sodium salt of dihydroxy-tartaric acid also loses carbon dioxide (and water) when heated in the *dry state*, and changes over into sodium tartronate. It is difficult to picture the movements of the sodium atoms in this reaction, on the basis of Equations 2 and 3. Kekulé must have felt this inadequacy, for he devoted much time to a study of the behavior of sodium dihydroxy-tartrate. On one occasion he heated the salt for over 800 hours, with more than 35 weighings. Fenton also made a painstaking investigation of this salt.<sup>4</sup>

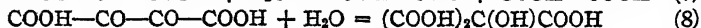
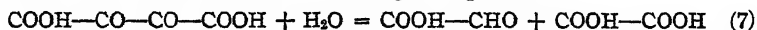
A satisfactory explanation of the conversion of dihydroxy-tartaric acid into tartronic acid must, of course, explain equally well the entirely similar transformation of its salt. Such an explanation has been found by noting the similarity in structure between dihydroxy-tartaric acid and benzil.

### Comparison of Dihydroxy-tartaric Acid and Benzil.

Benzil is an  $\alpha$ -diketone; likewise, dihydroxy-tartaric acid is its dehydrated form (2). In fact, dihydroxy-tartaric acid reacts with phenylhydrazine, taking up two mols. Benzil, treated with moderately concentrated alkalis, undergoes two different reactions simultaneously, *viz.*, rupture into benzaldehyde and benzoic acid, and rearrangement into benzilic acid



In the course of the present work, it was found that dihydroxy-tartaric acid, when acted upon by alkalis, behaves quite similarly. Rupture occurs, with production of oxalic and glyoxalic acids; and tartronic acid is also formed together with carbonic acid. Analogy clearly points to a primary rearrangement, in this latter case, to *carboxy-tartronic acid*, which then loses carbon dioxide according to Equation 1.



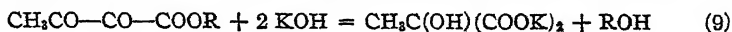
<sup>3</sup> Fenton and Ryffel, *J. Chem. Soc.*, 81, 426 (1902).

Fenton, *ibid.*, 87, 813 (1905).

<sup>4</sup> Fenton, *J. Chem. Soc.*, 74, 71 (1898). Kekulé (Ref. 2) promised a further investigation, which never appeared in print.

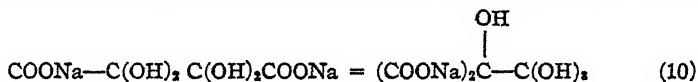
The only essential difference between the behavior of benzil and dihydroxy-tartaric acid lies in the fact that the CO groups in the latter substance are hydrated (cf. 4), and consequently neither water nor alkali is required to be added, so that both rupture and rearrangement may take place upon simple heating, *as in fact they do*. The details will be found in the experimental section of this paper.

The view that the formation of tartronic acid, in the above reactions, is due to a primary rearrangement, finds confirmation in the behavior of diketo-butyric acid.<sup>5</sup> This acid is known only in the form of an ester; when the ester is hydrolyzed by alkali, methyl-tartronic acid results.



It cannot be decided, in this case, whether methyl or carboxyl has shifted, the result being the same in either event. In the case of dihydroxy-tartaric acid, carboxyl is the only group that can shift. Nor is such a movement without analogy. Phenyl-oxypivalic ester, when heated with phosphorus pentoxide shifts a COOR group.<sup>6</sup>

When sodium dihydroxy-tartrate is heated, the shifting group is COONa



and we can thus understand why this salt loses carbon dioxide and water *simultaneously* when it is carefully heated (see experimental section). The carbon dioxide comes from the newly formed ortho-carboxyl group,  $-\text{C}(\text{OH})_2$ , not from the pre-existing, neutralized groups.

The two characteristic reactions which dihydroxy-tartaric acid undergoes simultaneously, *viz.*, rupture and rearrangement (7 and 8), like all simultaneous reactions, may have their relative velocities profoundly influenced by experimental conditions. Weak alkali, acting without undue increase in temperature, gives chiefly rearrangement, and only about 6% of the acid is ruptured. Stronger alkali, aided by heat, will increase the velocity of the rupturing process so that 50% or more of oxalic acid may be found. Heat, without alkali, produces rupture only to the extent of about 1%.

It is a striking phenomenon that rearrangement should be the preferred mode of adjusting the valence or electronic strains in such a complex molecule. It is equally suggestive that rearrangement occurs without the aid or influence of reagents.

<sup>5</sup> Denis, *Am. Chem. J.*, **38**, 589 (1907).

Latham, *Chem. Zentr.*, [II] 1908, 1050.

<sup>6</sup> Blaise and Courtot, *Bull. soc. chim.*, [3] **35**, 362 (1896). The same authors describe another case of carboxyl shift, *ibid.*, p. 969. Cf. Tiffeneau, *Rev. gen. sci.*, **12**, 588 (1907) for a discussion of this type of rearrangement.

## Experimental Part.

**Preparation of Sodium Dihydroxy-tartrate.**—Crude nitro-tartaric acid, as obtained after filtration from the sulfuric acid mixture<sup>7</sup> is stirred into a thin paste with cracked ice, and solid sodium carbonate added until the solution is nearly neutral. If too much has been added, make slightly acid with acetic acid. Under no circumstances must sodium *hydroxide* be used, as both nitro-tartaric and dihydroxy-tartaric acids are decomposed by it. The solution is allowed to stand, preferably immersed in cold water, for about 2 days. Sodium dihydroxy-tartrate deposits slowly, and may be filtered off from time to time. It should be thoroughly washed on the filter, and spread out in a thin layer for rapid drying. Yield, from 100 to 125% of the weight of tartaric acid taken.

As thus obtained, the salt is pure enough for all practical purposes. Previous investigators have failed to note the enormous tendency of this salt to occlude other salts, and their analytical data must therefore be regarded as uncertain. In fact, it may be doubted whether anyone has ever had a *pure* specimen of sodium dihydroxy-tartrate under observation. The best that I have been able to obtain was secured by redissolving 100 g. in just sufficient 3 *N* hydrochloric acid, and precipitating by an equal volume of 3 *N* sodium acetate; the precipitate was washed, first by decantation and then by suction, with 13 liters of water. The washing was continued long after the filtrates failed to give an opalescence with silver nitrate. The air-dried product contained 0.158% sodium chloride. When the hydrochloric acid was replaced by sulfuric, much larger amounts of sulfate were occluded.

**Composition**—The following data were obtained from the product just described, and have been corrected for sodium chloride content:

Loss on heating to ° C.		%.	Ignition residue (Na <sub>2</sub> CO <sub>3</sub> ). %.
150	Very slow	37.85	39.97
150	Very slow	37.85	40.00
165	Slow	37.75	39.95
170	Rapid	37.78	40.02
75	5 hours	2.05	...
96-97	40 hours	2.00	...
96-97	40 hours	2.06	...
Calculated for Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·2 H <sub>2</sub> O.			2.5 H <sub>2</sub> O.
3 H <sub>2</sub> O + CO <sub>2</sub> .....		37.40	39.48
Na <sub>2</sub> CO <sub>3</sub> .....		40.43	39.10

These data agree well with a water content of 2 mols., and not with 2.5 mols as claimed by Fenton. The rate of loss in weight on heating is very irregular; samples heated side by side varied widely on intermediate weighings.

<sup>7</sup> THIS JOURNAL, 43, 578 (1921).

**Oxidation by Permanganate.**—Fenton has proposed to use sodium dihydroxy-tartrate for the quantitative estimation of sodium, employing the potassium salt as reagent. The precipitated sodium salt is to be oxidized with permanganate. The method offers considerable advantages, as each atom of sodium requires 3 equivalents of oxygen. Fenton found, however, that the actual amount of oxygen consumed was always somewhat less than 3 equivalents. Part of this is accounted for by the occlusion referred to above. There are also irregularities in the action of the permanganate itself, and these were investigated during the present study.

It was found that these irregularities were caused entirely by partial formation of tartronic acid; for whereas solutions of dihydroxy-tartaric acid, freshly made and kept quite cold, used up exactly 3 oxygen equivalents, the same solutions after heating until all the dihydroxy acid had been converted into tartronic acid required but little more than two equivalents. This can be accounted for by the loss of some volatile product, such as formaldehyde or carbon monoxide. Formaldehyde was carefully sought for, but not found.

Quantitative and consistent results were obtained by first oxidizing with permanganate in alkaline solution, then completing in acid with excess of permanganate, using oxalic acid to secure the end point. As a reliable method of determining sodium will have considerable value, a few details will be given here; it is quite likely that the interference caused by occlusion can be minimized or obviated.

Using 0.5000 *N* permanganate solution, direct titration in cold acid solution gave, with samples of about 0.4 g. average weight, 99.8, 95.9, 94.7, 96.1, 93.0 and 94.3%.

Direct titration after boiling with dil. sulfuric acid, gave 62.0, 69.0, 63.7 and 73.5%.

Addition of sodium hydroxide, after boiling sample, before boiling, and together with permanganate followed by boiling respectively, then acidifying after excess of permanganate had acted hot, then finishing with oxalic acid, gave 100.1, 99.8 and 99.9%.

A final series was then made, using 0.1000 *N* permanganate with the following series of manipulations, in order: add dil. sodium hydroxide solution, heat, add excess of permanganate, boil for a few minutes, cool slightly, acidify with dil. sulfuric acid, add 0.1 *N* oxalic acid solution gradually, with boiling, until all of the manganese dioxide has gone into solution, cool slightly, and finish with permanganate. The sample (0.1059 g.) used 24.30-24.35-24.10-24.20-24.10 cc. of permanganate. Calculated, 24.25 cc.

#### **Loss of Carbon Dioxide on Heating Sodium Dihydroxy-tartrate.**—

It was shown above that the salt may be heated for nearly two days without any loss except absorbed moisture, below 97°. No carbon dioxide is given off. At or very near 100°, the substance loses weight again. Kekulé ran his tests "im dampfschrank." At this temperature weeks are required to reach constant weight. At 110° the process had not completed itself after 5 days. At 150° to 160°, a single hour suffices.

In all cases, carbon dioxide makes its appearance simultaneously with water, in agreement with Kekulé's observations. In one test the salt was heated in a boat within a tube passing through a Freas air-bath; a current of washed, dried air traversed the tube and a trap containing lime water. A temperature equilibrium at 105° was established before introducing the boat. The lime water became turbid within 2 minutes.

Attempts were made to measure the ratio of loss of water to that of

carbon dioxide; but owing to the irregularity in the rate of total loss referred to above, no results of value were obtained.

**Formation of Oxalic and Glyoxalic Acids.**—If the rupturing process shown in Equation 7 accompanies the rearrangement of sodium dihydroxy-tartrate into sodium tartronate, the heated salt must be *acidic* in proportion to such rupture, since a new carboxyl group is formed.

Twenty-five g. of salt was heated to 160° for 1 hour, and required 5.5 cc. of 0.1 *N* sodium hydroxide solution to neutralize. This corresponds to 0.55% rupture. Twenty-five g. of salt was next boiled with 100 cc. of water until no more gas was given off; the mixture was allowed to cool and the volume restored, and boiled again. Twelve and one-tenth cc. of alkali was needed to neutralize the acid, equivalent to 1.2% rupture.

The two lots were combined, and phenylhydrazine acetate added. A yellow precipitate formed promptly, insoluble in dil. hydrochloric acid, soluble in sodium carbonate, slightly soluble in ether, easily soluble in alcohol, m. p. 137° (uncorr.), thus identifying it as the phenylhydrazone of glyoxalic acid.

The quantitative estimation of the amount of oxalic acid formed proved very troublesome. This was due to the presence of large amounts of tartronic acid, which also gives an insoluble calcium salt. After the details of the permanganate method for determining tartronic acid (see above) had been worked out, it was possible to use this method on a mixture of calcium tartronate and oxalate, and from the amount of oxygen consumed calculate the proportion of each salt present.

There were some additional difficulties. Calcium tartronate has a different composition when precipitated hot than when formed in the cold. It is also markedly soluble in excess of calcium chloride in the cold, and comes down very slowly when these solutions are boiled. It is therefore necessary to precipitate the mixed acids very slowly and carefully from boiling solutions, and to avoid excess of calcium chloride as much as possible. Nor is this all; the mixed precipitates must be dried at about 170–180°; but calcium oxalate, thus dehydrated, is enormously hygroscopic. Any water present in the sample will decrease the amount of permanganate required, and thus increase the apparent percentage of oxalate.

The results obtained may be summarized briefly. Two samples of sodium dihydroxy-tartrate were carefully warmed with a slight excess of 3 *N* sodium hydroxide solution until dissolved. The yields of oxalic acid were 5.9 and 6.4% respectively. Ten g. of salt was next dissolved in a slight excess of 3 *N* hydrochloric acid, and the solution added quickly and without cooling to a considerable excess of 6 *N* sodium hydroxide solution. The yield of oxalic acid was 9.4%.

Finally, 18 g. of nitrotartaric acid, dissolved in 50 cc. of alcohol, was slowly run into a solution of 15 g. of sodium hydroxide in 150 cc. of alcohol, with water cooling. A yield of 51% of oxalic acid was obtained.

From this last lot, it was possible to secure a small amount of glycolic acid as calcium salt.<sup>8</sup>

<sup>8</sup> Böttinger, *Ber.*, 13, 1932 (1880), has shown that glyoxalic acid is unstable in the presence of alkalis, and goes over into a mixture of glycolic and oxalic acids. He states that the recovery of the glycolic acid is very difficult, which can be confirmed. Cf. Debus, *Ann.*, 338, 322 (1905) for a careful study of this reaction.



### Summary.

1. Dihydroxy-tartaric acid, considered as a diketone, has a structural resemblance to benzil.
2. This resemblance extends to the reactions of the two compounds.
3. The conversion of dihydroxy-tartaric acid and its salts into tartronic acid is an analog of the rearrangement of benzil to benzilic acid.
4. The composition and behavior of sodium dihydroxy-tartrate are discussed.
5. Data are given which will help in the development of the method proposed by Fenton for the direct quantitative estimation of sodium.

BERKELEY, CALIFORNIA.

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[CONTRIBUTION NO. 6 FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY.]

### SPIRO-PYRIMIDINES. III. CONDENSATION OF CYCLOPROPANE-1,1-DICARBOXYLIC ESTER WITH UREAS.

BY ARTHUR W. DOX AND LESTER YODER.

Received May 19, 1921.

The preparation of *spiro*-pyrimidines containing 4- and 6-membered hydrocarbon rings has been described in our previous papers.<sup>1</sup> The corresponding 3-membered ring with one of its carbon atoms identical with the 5-carbon atom of barbituric acid was cited as the simplest derivative of this type. Certain difficulties were encountered in preparing such derivatives, hence the discussion was reserved for a later paper. The condensation of cyclopropane-1,1-dicarboxylic ester with urea was readily effected, but the product was so entirely different in its properties from the corresponding cyclobutane and cyclohexane derivatives that it was thought advisable to repeat the work. It has now become evident that a very stable polymer is formed in this reaction, and although its constitution has not been definitely established, it seems advisable to publish the results thus far obtained, for the reason that further work along this line is not contemplated.

#### Preparation of Ethyl Cyclopropane-1,1-dicarboxylate.

This substance has been prepared by Perkin.<sup>2</sup>

In view of the tediousness of Perkin's process and the smallness of the yield, we undertook to apply the method by which we obtained good results in the preparation of cyclobutane-1,1-dicarboxylic ester. According to Perkin there is in this case, much less tendency toward the formation of the open chain tetracarboxylic ester.

<sup>1</sup> Dox and Yoder, *THIS JOURNAL*, 43, 877-84, 1366-71 (1921).

<sup>2</sup> Perkin, *Ber.*, 17, 54-9 (1884); *J. Chem. Soc.*, 47, 808 (1885); *ibid.*, 51, 849-53 (1887).

A mixture of 310 g. of ethylene bromide and 255 g. of ethyl malonate was placed in a flask provided with a reflux condenser and a mechanical stirrer. The flask was immersed in a bath of water maintained at about 80°. By means of a dropping funnel, a solution of 73 g. of sodium in 1100 cc. of absolute alcohol was slowly added during the course of 2½ hours. After the mixture had been heated and stirred for 5 hours the reaction product was neutral to litmus. Most of the alcohol was then distilled, while the solution was stirred continuously. A test portion now showed a slightly alkaline reaction, and hydrochloric acid was added to make the mixture exactly neutral. On the addition of water, the sodium bromide dissolved and a yellow oil separated. The latter was extracted with ether. The yield of crude oil was 237 g. On fractionation 148 g. or 60% of the oil distilled between 200° and 220°. This was fractionated twice and finally yielded 120 g. of a product which distilled between 214° and 216° (corr.) at 748 mm. pressure. Perkin reports a boiling point of 208–10° at 720 mm. Our yield of pure product was 40%, as compared with Perkin's yield of 27–9%.

### Condensation with Urea.

To a solution of 3.7 g. of sodium in 65 cc. of absolute alcohol, 10 g. of ester and 5 g. of urea were added and the mixture was heated for 4 hours in an autoclave at 105°. The white insoluble product was collected on a filter, then dissolved in water and acidified with hydrochloric acid. A voluminous white amorphous precipitate immediately formed. It was insoluble in water, acids and organic solvents, but slowly soluble in caustic alkalis. The yield was 3.5 g. or 42%. On heating the substance it charred at a high temperature without melting. It is precipitated from its alkaline solutions by acetic acid, or by carbon dioxide. Repeated attempts to obtain it in crystalline form by slow neutralization of the alkaline solution or by slow dilution of its solution in conc. sulfuric acid were unsuccessful. The product was invariably amorphous.

*Analysis.* Subs., 0.2, 0.2:  $\text{NH}_3$ , 26.16, 26.13 cc. of 0.1 *N*. Calc. for  $\text{C}_4\text{H}_6\text{N}_2\text{O}_3$ : *N*, 18.18. Found: 18.05, 18.03.

The insolubility and amorphous character of the above product as contrasted with the solubility, crystalline form and sharp melting points of the corresponding cyclobutane and cyclohexane derivatives justify the assumption that a polymerization has occurred. Experiments were conducted to determine whether such polymerization could be avoided by altering the conditions of the condensation. If the polymerization were due to the hydrochloric acid used in liberating the product from its sodium salt, an organic acid should obviate this difficulty. It was found, however, that treatment of the original sodium salt with acetic acid and even with carbon dioxide gave the same product as before. The high temperature of the autoclave or the excess of sodium ethylate did not account for polymerization, since the same product was obtained when the condensation was performed on a steam-bath under a reflux condenser, using 1 mole of sodium instead of 3. In every experiment performed the product obtained was amorphous, insoluble in water, acids and organic solvents, and infusible.

A cyclopropane ring might conceivably polymerize in a number of ways. The simplest possibility is the union of two molecules to form a cyclohexane ring. Such a product would yield on complete hydrolysis of the ureide groupings and loss of one carbon dioxide from each of the carbons carrying two carboxyls, hexahydro-phthalic or hexahydro-terephthalic acid. Again the cyclopropane-*spiro*-barbituric acid might rearrange into vinyl-barbituric acid and then polymerize into a cyclobutane ring with 2 barbituric acid groups attached. The acids which would result from hydrolysis of such a product have not been prepared. Still again, 3 molecules of vinyl-barbituric acid might polymerize with formation of a cyclohexane nucleus. In fact, a number of other possibilities still more remote might be cited.

### Hydrolysis of the Polymer.

Long boiling of the polymer with conc. hydrochloric acid did not alter it. After 3 hours' heating in a sealed tube at 180° with conc. hydrochloric acid, the polymer was recovered quantitatively and the filtrate showed only a trace of ammonium chloride. It was found, however, that hydrolysis can be effected by boiling it with 10% sodium hydroxide for a long time. The substance goes into solution by the time the boiling point is reached, but the evolution of ammonia does not cease until the solution has been boiled for several hours. After complete hydrolysis, as shown by the absence of ammonia and the failure of a test portion, when acidified, to give a precipitate, the solution was acidified with hydrochloric acid and evaporated. Most of the sodium chloride was removed by crystallization and, finally, a sirupy acid was obtained. On heating this in an oil-bath to 200° a copious evolution of carbon dioxide occurred. The residue was then dissolved in water, decolorized with charcoal and crystallized twice. The white crystals, thus obtained, were readily soluble in water and in alcohol, difficultly soluble in ether and in chloroform, and had a strongly acid taste. The melting point was 152° (corr.); 0.1 g. required 11.97 cc. of 0.1 *N* sodium hydroxide for neutralization. The neutralization equivalent was 88. This corresponds to a dibasic acid of molecular weight 176, and is in close agreement with the various acids  $C_8H_{12}O_4$  theoretically possible from polymerization of cyclopropane-carboxylic acid. Of the hexahydro-phthalic acids mentioned above, the only one that approximates this melting point is *cis*-hexahydro-terephthalic acid which melts at 161°. This, however, undergoes a rearrangement into the *trans* acid on heating with hydrochloric acid at 180°. Our acid remained unchanged after this treatment.

### Mono-amide of Cyclopropane-1,1-dicarboxylic Acid.

From the mother liquor of the condensation product, after precipitation of the polymer by acid, 2 g. of a crystalline acid melting at 195° was obtained. It was readily

soluble in water and in alcohol. The nitrogen content and the neutralization equivalent correspond with the calculated values for the mono amide of cyclopropane-1,1-dicarboxylic acid.

*Analyses.* Subs., 0.2, 0.2:  $\text{NH}_3$ , 16.1, 16.1 cc. of 0.1 *N*. Calc. for  $\text{C}_5\text{H}_7\text{NO}_3$ : N, 10.85. Found: 10.99, 10.99.

Subs., 0.1: NaOH, 15.72 cc. 0.1 *N*. Calc. neutral equiv. for  $\text{C}_5\text{H}_7\text{NO}_3$ : N, 129. Found: 127.

#### Di-amide of Cyclopropane-1,1-dicarboxylic Acid.

This was easily prepared by shaking the ester with aqueous ammonia. Five g. of ester and 20 cc. of conc. ammonium hydroxide were placed in a stoppered bottle and shaken 18 hours in a shaking machine. By that time the oily layer had completely disappeared and an abundance of white prismatic crystals had formed. The yield was 3.4 g. or 84%. The substance melts at  $198^\circ$ . It is moderately soluble in water and readily soluble in alcohol.

*Analyses.* Subs., 0.2, 0.2:  $\text{NH}_3$ , 31.61, 31.21 cc. of 0.1 *N*. Calc. for  $\text{C}_5\text{H}_5\text{N}_2\text{O}_2$ : N, 21.80. Found: 21.84, 21.56.

#### Condensation of the Di-amide with Diphenyl Carbonate.

Einhorn and Ladisch<sup>3</sup> prepared veronal by the condensation of diethyl-malonyl amide with diphenyl carbonate at  $200^\circ$ . It was thought that the di-amide described above might condense in the same way, possibly without polymerization of the product. One g. of diamide and 2 g. of diphenyl carbonate were intimately mixed and heated in an oil-bath at  $190$ – $200^\circ$ . A short test-tube was used and this was immersed up to the flange so that the phenol distilled as fast as it was formed. After 9 hours' heating the reaction mixture was extracted with dil. sodium hydroxide solution and filtered from the insoluble phenyl carbonate. When the filtrate was acidified, an amorphous white precipitate was obtained which showed all the properties of the polymer already described.

#### Condensation of the Ester with Guanidine.

A mixture consisting of 1.2 g. of sodium dissolved in 50 cc. of absolute alcohol, 10 g. of ester and 5 g. of guanidine carbonate was heated under a reflux condenser for  $5\frac{1}{2}$  hours. The white amorphous mass obtained was evaporated on a steam-bath to remove most of the alcohol and then taken up with water. An opalescent solution resulted which became more and more cloudy on standing. The addition of acetic acid caused the immediate precipitation of the free base. It was washed thoroughly with water, alcohol and ether, then dried at  $100^\circ$ . The yield was 3.5 g. or 43%. The substance showed the same properties as the corresponding urea derivative except that it was soluble in mineral acids as well as in alkalis.

Subs., 0.2, 0.2:  $\text{NH}_3$ , 37.6, 37.6 cc. 0.1 *N*. Calc. for  $\text{C}_5\text{H}_7\text{N}_3\text{O}_2$ : N, 27.45. Found: 26.32, 26.32.

#### Condensation of the Ester with Thio-urea.

To a solution of 3.7 g. of sodium in 65 cc. of absolute alcohol, 10 g. of

<sup>3</sup> Einhorn and Ladisch, *Ann.*, 359, 184 (1908).

este and 5 g. of thio-urea were added and the mixture heated for 4 hours at  $105^{\circ}$ . The condensation product insoluble in the alcoholic solution was collected on a filter, then dissolved in water. On acidifying the solution with hydrochloric acid, a copious white amorphous precipitate formed at once. It was somewhat soluble in hot water and slightly more soluble in hot alcohol but could not be obtained from either solvent in crystalline form. The yield was 7 g. or 76%.

Subs., 0.2, 0.2:  $\text{NH}_3$ , 22.76, 22.65 cc. 0.1 N. Calc. for  $\text{C}_8\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ : N, 16.47. Found: N, 15.93, 15.85.

Subs., 0.2:  $\text{BaSO}_4$ , 0.2808. Calc.: S, 18.80. Found: 19.28.

### Summary.

1. Cyclopropane-1,1-dicarboxylic ester condenses with urea, guanidine and thio-urea to form stable, amorphous products. From comparison with the corresponding cyclobutane and cyclohexane derivatives it is apparent that these products are polymers.

2. Hydrolysis of the urea polymer, followed by elimination of carbon dioxide, gave a crystalline acid with melting point  $152^{\circ}$  and molecular weight 176 (by titration). Of the acids,  $\text{C}_8\text{H}_{12}\text{O}_4$ , theoretically possible from hydrolysis of a dimer only the hexahydrophthalic acids are known. It is probable that a cyclopropane-1.5-*spiro*-barbituric acid first formed undergoes rearrangement to vinyl-barbituric acid which then polymerizes. The product would then be a cyclobutane-dibarbituric acid, which on hydrolysis and loss of 2 molecules of carbon dioxide would yield cyclobutane-1,2- or -1,3-di-acetic acid, both of which could exist in *cis* and *trans* forms. It is probable that the polymer is not a *spiro* derivative but rather cyclobutane-dibarbituric acid.

DETROIT, MICHIGAN.

[CONTRIBUTION FROM THE BUREAU OF PLANT CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

## CHANGES IN THE COMPOSITION OF PAPRIKAS DURING THE GROWING PERIOD.

By A. F. SIEVERS AND J. D. MCINTYRE.

Received June 9, 1921.

The change in chemical composition of plants during their growth and development has always been an inviting field of research for the chemist and plant physiologist. Especially is this true in connection with fruits, vegetables and drugs. Much work has been done in this direction, particularly when some definite chemical compound is of predominating influence in determining the quality of the product. As examples, one might mention the development of sugars in the orange, sugar-beet, sweet-corn and sweet potato; citric acid in the lemon; volatile

cils in aromatic herbs; and alkaloids or other active principles in medicinal plants. Such studies are of more than mere scientific interest in that they frequently serve to show at what stage of growth a product should be harvested in order to assure maximum quality and the extent to which lack of care in gathering may affect the general quality of the harvest.

The red peppers, which are widely used as condiments, depend to a varying degree on their pungency as a measure of quality. The investigation here recorded was undertaken for the purpose of tracing the development of the pungent principle and sugar in the paprika, a large fruited variety of *Capsicum annuum*, L. The literature records a great deal of work on the composition of paprikas but the investigations appear to deal mostly with the composition of the several parts of the fruit and the effect of additions of foreign matter on such composition. No systematic study of the fruit from its early formation to its maturity appears to have been recorded.

The paprikas were grown at Arlington, Virginia, and at several intervals of the growing season samples of 6 different sizes of fruit were picked. Since a single plant will bear fruit of all stages of development at one time, the above method appeared to be the most feasible means of securing representative samples of fruit of the several stages. The smallest specimens picked included fruit under 25 mm. in length, while the largest specimens were 100 mm. or more in length. Table I shows the average size and weight of the several samples collected.

TABLE I.

## AVERAGE SIZE AND WEIGHT OF PAPRIKAS AT SIX STAGES OF GROWTH.

Stage.	Length. Mm.	Diameter. Mm.	Weight. G.	Color.
1	less than 25	7.3	1.89	green
2	25 to 37	10.2	3.10	green
3	37 to 50	14.1	7.77	green
4	50 to 75	18.5 <sup>a</sup>	10.77	a few were slightly red
5	75 to 100	17.6	14.86 <sup>b</sup>	about one-half were red
6	more than 100	...	....	all dark red

<sup>a</sup> At this stage the maximum diameter was attained. Upon further development the fruit began to shrink or shrivel somewhat; hence, diameter measurements of the last sample were not taken.

<sup>b</sup> The maximum weight is reached at this stage. The fruit loses considerably in weight as it matures.

The fruit was carefully freed from adhering soil, and after the stems and calyxes had been removed was spread out thinly to dry in a well ventilated room. The dry pods, consisting of shells, placenta and seeds were then ground and passed through a 40-mesh sieve. The samples were analyzed for moisture, ash, alcohol extract, volatile and non-volatile ether extract and reducing and total sugars. The analyses were made according to the Official and Provisional Methods of Analysis, Bureau of Chemistry *Bulletin* 107 (revised), except in the case of the sugars which were extracted accord-

ing to a modified method and then determined by the official gravimetric method. A summary of the results of the analyses is shown in Table II.

TABLE II.

## RESULTS OF THE ANALYSES OF PAPRIKAS AT SIX STAGES OF GROWTH.

Stage.	Mois- ture. %.	Ash. %.	Ether extract.			Alcohol extract. %.	Sugars.	
			Volatile. %.	Non-volatile. %.	Total. %.		Reducing. %.	Total. %.
1	8.46	8.13	0.19	1.95	2.14	18.72	5.81	11.90
2	6.79	7.72	0.17	2.47	2.64	17.03	5.81	13.81
3	7.63	7.57	0.22	4.82	5.04	18.25	6.27	14.72
4	7.19	7.00	0.27	5.24	5.51	19.15	5.90	13.92
5	7.21	6.85	0.24	6.35	6.59	19.24	6.42	13.32
6	7.16	6.78	0.85	8.33	9.18	21.15	8.59	14.39

It will be noted that the ash and ether extract show a definite change through the several stages. The former decreased from 8.13 to 6.78%. The ash was practically all soluble, only slight traces of insoluble matter being present. The total ether extract increased from 2.14 to 9.18% which is a very good indication of the development of the pungent principle. The volatile ether extract, which represents the volatile oil, increased from 0.19 to 0.85%, practically all the increase taking place during the end of the growing period. The alcohol extract shows no definite or decided change and the same may be said about the sugars. The percentage of both total and reducing sugars in the small immature paprikas is exceedingly high as compared with the amount present in the ripe fruit. There are considerable fluctuations in the sugar content during the several stages, due in some measure, possibly, to the tendency of sugars to undergo changes during the drying of the material. The outstanding fact to be noted from these analyses is the increase in the pungency as indicated by the ether extract.

As a rapid means of roughly determining the relative pungency of paprikas, it has been proposed to triturate a definite weighed quantity of the ground pepper in a mortar with sugar, the latter being added a little at a time until a small quantity of the mixture when placed on the tongue does not produce a distinctly pungent taste. This method is, of course, of no analytical value, but when applied to the above 6 samples of paprikas it gave a fair indication of the increase in pungency as the fruit matured. Thus, the quantity of sugar required to mask the pungency of 0.2 g. of the paprika from the first to the last stage was as follows: 0.39, 5.55, 5.52, 7.6, 12.48 and 32.2 g.

In conclusion it may be said that the ether extract is a fairly accurate measure of the maturity of the paprikas, but it is necessary that the normal ether extract of an average sample of such peppers be known for comparison. On the other hand, neither the sugar content nor the alcohol extract changes sufficiently or with such marked regularity as to indicate

the stage at which the fruit was picked. Furthermore, it is evident that even in cases where color is of no consequence and pungency is of first consideration, fully matured fruit must be used to obtain the maximum value.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]  
**DERIVATIVES OF ANTHRAQUINONE. ALIPHATIC THIO-ETHERS,  
 ERS, DITHIO-ETHERS, AND THIO-ETHER SULFONIC ACIDS.**

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Received June 10, 1921.

**Introduction.**

The original object in taking up the study of anthraquinone sulfonic acids was to obtain derivatives which could be used for their ready separation and identification. This object was only partially attained but the reaction tried proved interesting and the products obtained appeared worthy of study, so the investigation was shifted from its original purpose and extended in other directions.

On account of the instability of the esters of sulfonic acids the methods used for the identification of carboxy acids<sup>2</sup> were not promising and our efforts were directed to the replacement of the sulfonic groups.

It was known that the sulfonic acid group of  $\alpha$ -anthraquinone sulfonic acids can be replaced by methoxy<sup>3</sup> or phenoxy<sup>4</sup> groups, and that the resulting compounds  $C_{14}H_7O_2.OCH_3$  and  $C_{14}H_7O_2.OC_6H_5$  are crystalline and have definite, though rather high melting points. Hence it was thought that a compound of the type  $C_{14}H_7O_2.SR$  would be of service. *N*-butyl mercaptan was used as being readily available, and it was thought probable that the compound  $C_{14}H_7O_2.SC_4H_9$  would have a low melting point, since sulfur compounds usually melt lower than the corresponding oxygen compounds, and since butyl derivatives are apt to melt considerably lower than methyl, and much lower than phenyl. The desired reaction was found to take place readily, although not quantitatively, when the sulfonic acid group is in the  $\alpha$ -position. The resulting compounds were found to have convenient melting points suitable for the identification of anthra-

<sup>1</sup> The work on the 1,5-compounds is from the Doctor's dissertation (1920) of Colin M. Mackall and that on the 1,8-compounds from that of George E. Miller (1920); the  $\alpha$ -derivatives were prepared by the other author with some assistance from W. S. Hoffman of this Laboratory and A. T. Frascati in the Laboratory of E. I. du Pont de Nemours and Company.

<sup>2</sup> THIS JOURNAL, 39, 124, 304, 701, 1727 (1917); 41, 75 (1919); 42, 1043 (1920); and 43, 629 (1921).

<sup>3</sup> Bayer and Co., Ger. pat. 156,762.

<sup>4</sup> Bayer and Co., Ger. pat. 158,531.



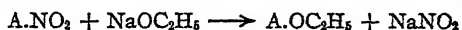
quinone- $\alpha$ -sulfonic acid, and anthraquinone-1,5- and -1,8-disulfonic acids.

Our study has been extended to the derivatives of other mercaptans.

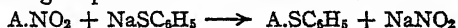
### Historical.

Anthraquinone aliphatic thio-ether sulfonic acids and dithio-ethers may be prepared by the action of aliphatic mercaptans on anthraquinone sulfonic acids in alkaline solution.<sup>5</sup> In this way Bayer and Company prepared anthraquinone-1-ethyl-thio-ether-5-sodium sulfonate and 1,5-diethyl-thio-ether.

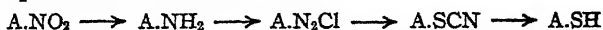
Gattermann<sup>6</sup> has shown that the nitro group is replaceable by the alkoxy group when treated with sodium alcoholate, thus,



representing the anthraquinone residue by A. He attempted to carry out the analogous reaction with aliphatic mercaptans in order to obtain anthraquinone thio-ethers, but was hindered by the reduction of the nitro group to the amino group. On the other hand, he found that treatment with alkali aromatic mercaptides readily caused a quantitative replacement of the nitro group with the formation of aromatic thio-ethers.



Gattermann<sup>7</sup> has also prepared anthraquinone aliphatic thio-ethers and thio-ether sulfonic acids indirectly by diazotizing amino-anthraquinones, or amino-anthraquinone sulfonic acids in conc. sulfuric acid. Subsequent treatment of the diazo compound with potassium thiocyanate yielded anthraquinone thiocyanate which on boiling with alcoholic potash gave the mercaptan, which with alkyl halide yielded the thio-ether or thio-ether sulfonic acid. In this way he prepared anthraquinone- $\alpha$ -methyl-thio-ether; anthraquinone- $\alpha$ -ethyl-thio-ether; anthraquinone-1-methyl-thio-ether-5-potassium sulfonate; and anthraquinone-1-methyl-thio-ether-8-potassium sulfonate, thus,



### Outline of Present Investigation.

We have found that anthraquinone- $\alpha$ -sulfonic acid, and the 1,5- and 1,8-disulfonic acids, on heating with aliphatic mercaptans in alkaline solution, react readily to form anthraquinone thio-ethers, thio-ether sulfonic acids, and dithio-ethers, the sulfonic acid groups being replaced in turn.

This reaction takes place with great ease at 100° provided the concentrations are right. The formation of the product from the  $\alpha$ -sulfonate

<sup>5</sup> Bayer and Co., Ger. pat. 224,589.

<sup>6</sup> Bayer and Co., Ger. pat. 75,054.

<sup>7</sup> *Ann.*, 393, 113 (1912).

can be noticed within 2 to 10 minutes after adding the mercaptan. With the 1,5-disulfonate, the separation of the thio-ether monosulfonate begins within a few minutes on account of the very slight solubility of these compounds, while with the 1,8-disulfonate the reaction follows the same course except that the half-way product is much more difficult to obtain, on account of its greater solubility which favors the second stage of the reaction.

Gattermann found that  $\alpha$ -C<sub>14</sub>H<sub>7</sub>O<sub>2</sub>NO<sub>2</sub> reacts readily with potassium thiophenate, KSC<sub>6</sub>H<sub>5</sub>, to give  $\alpha$ -A-SC<sub>6</sub>H<sub>5</sub>. We have endeavored to replace the sulfonic group by using phenyl mercaptan in the same way as the alkyl mercaptans but so far without result, though benzyl and *p*-nitrobenzyl mercaptans react readily under the regular conditions to give excellent yields of the corresponding thio-ethers.<sup>8</sup>

Several experiments have been made in the hope of finding the determining factor. The sodium salt of thioglycolic acid reacts readily but the sodium salt of thiolbenzoic acid does not. In this case the mixture was heated for about 40 hours but no sulfur dioxide was evolved on acidifying a test portion, showing that no sulfite had been formed. The thiolbenzoic acid could be recovered unchanged. This was tried with the 1,5-disulfonate for the same time but with similar negative results; however, there was some indication of a reaction with the 1,8-disulfonate though it had not gone far in 40 hours' heating.

In the hope of finding some compound with about the same acid strength as the aliphatic mercaptans, *m*-aminophenol was tried. This and the sulfonate were boiled with excess of caustic soda solution but there was no evidence of a reaction.

As the  $\alpha$ -sulfonic acid group is somewhat more reactive than the  $\beta$ -group in naphthalene, sodium  $\alpha$ -naphthalene sulfonate was boiled with butyl mercaptan and caustic soda solution, but no reaction took place.

### The Compounds Obtained.

The anthraquinone thio-ethers and dithio-ethers are insoluble in water, slightly soluble in alcohol and soluble in benzene, the solubility in benzene increasing with the size of the alkyl group. When crystallized from benzene they form lustrous crystals varying in color from light yellow to red.

The corresponding sulfones are high melting, slightly yellow crystalline powders.

The anthraquinone-thio-ether sodium sulfonates are moderately soluble in water, the derivatives of the lower mercaptans being more soluble than those of the higher mercaptans and the 1,8 salts being considerably more soluble than the corresponding 1,5 salts. They crystallize from water in

<sup>8</sup> Unpublished work of W. S. Hoffman.

orange or orange-red needles usually containing one molecule of water of hydration. Salts of other bases are highly colored, ranging from yellow through shades of orange to red and are mostly well crystallized.

In the 1,5 series of monobutyl-thio-ether sulfonates, the colors of the barium, strontium and calcium salts run in this order, the barium being deep red and the calcium salt orange, while in the corresponding 1,8 series the order of the colors is reversed.

### Experimental.

**Materials.**—The anthraquinone- $\alpha$ -sodium sulfonate, and anthraquinone 1,5- and 1,8-disodium sulfonates were obtained through the courtesy of E. I. du Pont de Nemours and Company. The methyl mercaptan was generated as required by dropping dimethyl sulfate into warm sodium hydrosulfide, which was prepared by warming crystallized sodium sulfide,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , to about  $90^\circ$  and saturating with hydrogen sulfide. The ethyl mercaptan was prepared in a similar manner using sodium ethyl sulfate. The propyl, butyl and *iso*-amyl mercaptans were prepared by the catalytic method of Kramer and Reid.<sup>9</sup>

### Analytical.

1. **Water of Hydration.**—One-g. samples were exposed to an atmosphere of 50% humidity<sup>10</sup> for 48 hours, then heated to constant weight in a vacuum at  $110^\circ$ , 2 to 4 hours being generally sufficient to remove all the water. Analyses for sulfur and metals were made on the dry samples.

2. **Sulfur.**—Sulfur was determined by means of the Parr bomb,<sup>11</sup> using a 0.2 g. sample and 5 g. of sodium peroxide, with subsequent precipitation of barium sulfate.

3. **Sodium, Barium, Strontium, Calcium, Nickel and Cobalt.**—One-half g. samples were ignited in a platinum crucible until the carbon was burned off as completely as possible. The residue was then evaporated with conc. sulfuric acid, and re-ignited with ammonium carbonate to constant weight. The metal was weighed as the sulfate.

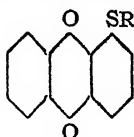
4. **Lead.**—Half-g. samples were ignited cautiously and the residue heated with nitric acid which was evaporated. The residue was evaporated with sulfuric acid and re-ignited with ammonium carbonate to constant weight, the metal being weighed as sulfate.

5. **Copper.**—The copper was precipitated in a faintly ammoniacal solution with hydrogen sulfide. The precipitate was filtered off, dried, ignited and weighed as cupric oxide.

<sup>9</sup> Kramer and Reid, *THIS JOURNAL*, 43, 880 (1921).

<sup>10</sup> A dead air humidor containing 44%  $\text{H}_2\text{SO}_4$  was used to obtain this humidity.

<sup>11</sup> Parr, *J. Ind. Eng. Chem.*, 11, 230 (1919).

I. Anthraquinone  $\alpha$ -Alkyl Thio-ethers.

One-fifth mole, or 62 g., of sodium anthraquinone  $\alpha$ -sulfonate was heated with 1400 cc. of water containing 0.5 mole of caustic soda and a little more than 0.25 mole of the desired mercaptan. The solubility of sodium anthraquinone  $\alpha$ -sulfonate is given by Dünschmann<sup>12</sup> as 5.1 g. per 100 cc. of boiling water but is diminished by the presence of the caustic soda, so that not quite all of the salt was in solution at the start. The methyl mercaptan was passed through in vapor form while the reaction mixture was heated to near its boiling point and mechanically stirred. The other mercaptans were added in liquid form, sometimes in portions, and the mixtures boiled under reflux. The acid character of the mercaptans is so weak that they readily distil out of the mixture even though it contains an excess of alkali. For this reason some excess of mercaptan was used, particularly of the more volatile ones. With propyl mercaptan 38 g. or 67% of the calculated amount of  $\alpha$ -C<sub>14</sub>H<sub>7</sub>O<sub>2</sub>.SC<sub>3</sub>H<sub>7</sub>, was obtained directly but the filtrate was boiled with 5 g. additional of mercaptan and 10 g. more of the product obtained, bringing the yield up to 85%.

The reaction takes place rapidly and considerable of the product can be observed within 2 to 10 minutes, but the mixtures were heated about 10 hours. The reaction mixtures were filtered hot and the sodium salts washed out with hot water. The anthraquinone-thio ethers were recrystallized from benzene or benzene and alcohol. The yields were good.

Details of several preparations are given in tabular form.

TABLE I.

PREPARATION OF	$\alpha$ -ALKYL	ANTHRAQUINONE	THIO-ETHERS, $\alpha$ -C <sub>14</sub> H <sub>7</sub> O <sub>2</sub> .SR.			
Alkyl. *	Sodium sulfonate.	Water. Cc.	NaOH. G.	Mercaptan. G.	Yield. G.	%.
Ethyl	20	400	4	5	9	50
Ethyl	62	1500	20	20	47	88
Propyl	62	1500	20	19	48	85
Butyl	62	1400	20	23	55	93
<i>iso</i> -Butyl	62	1400	20	20	42	81
<i>iso</i> -Amyl <sup>1</sup>	62	1400	20	26	53	86

TABLE II.

PROPERTIES AND ANALYSES<sup>13</sup> OF ALKYL ANTHRAQUINONE THIO-ETHERS,  $\alpha$ -C<sub>14</sub>H<sub>7</sub>O<sub>2</sub>.SR.

Alkyl.	M. p. ° C.	Calc. Sulfur. %.	Found. %.	Color and form.
Methyl	221	12.66	12.31	reddish-orange needles
Ethyl	184	11.62	11.51	orange nd.
Propyl	151	11.40	11.36	orange nd.
Butyl	112.5	10.82	10.77	yellowish-red nd.
<i>iso</i> -Butyl	144	10.82	10.98	yellow
<i>iso</i> -Amyl	86	10.33	10.57	orange

The melting point goes down as the weight of the alkyl group increases.

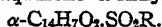
<sup>12</sup> Dünschmann, *Ber.*, 37, 331 (1904).

<sup>13</sup> Melting points and analyses by W. S. Hoffman.

Gattermann gives the melting points of the methyl and ethyl derivatives as 208° and 183°.

**Anthraquinone Thioglycolic Acid**,  $C_{14}H_7O_2.SCH_2COOH$ .—A mixture of 31 g. of sodium  $\alpha$ -anthraquinone sulfonate, 11.5 g. of thioglycolic acid, 10 g. of sodium hydroxide and 700 cc. of water was boiled for 11 hours. Crystals, 27 g., separated on cooling. These were filtered off and dissolved in hot water and the free acid precipitated by hydrochloric acid. They were recrystallized partly from nitrobenzene and partly from water and obtained as fine bright yellow needles, m. p. 243°, from which was prepared the sulfoxide, m. p. 239°; Gattermann gives m. p. 250° and 240°, respectively.

## II. Anthraquinone $\alpha$ -Alkyl Sulfones.



The sulfones were prepared by oxidizing the thio-ethers by pouring over them enough fuming nitric acid to dissolve them, and pouring the solution into hot water. They may be purified by recrystallization from acetic acid. When prepared from pure thio-ethers they are obtained pure at the start and their melting points are not raised by recrystallization. All of them are slightly yellowish-white.

TABLE III.  
ALKYL ANTHRAQUINONE SULFONES,  $\alpha-C_{14}H_7O_2.SO_2R$ .

Alkyl.	M. p. °C.	Calc. %.	Sulfur.	Found. %.
Methyl	254	11.20		10.88
Ethyl	211.5	10.68		10.74
Propyl	204.5	10.20		10.30
Butyl	150	9.77		10.00
<i>iso</i> -Butyl	190	9.77		9.97
<i>iso</i> -Amyl	133	9.37		9.56

Gattermann gives the methyl and ethyl sulfones as melting at 251° and 210°.

## III. Experiments with Sodium $\beta$ -Anthraquinone Sulfonate.<sup>14</sup>

Only preliminary experiments have been made, as it was soon found that this subject must be left for further study. When the sulfonic acid group is in the  $\beta$ -position the replacement by the mercaptan residue takes place with much greater difficulty, if at all; such small quantities, only about 1.3%, of thio-ethers have been obtained, when the experiment is tried in the usual manner, that it is not certain whether the product is produced from the  $\beta$ -sulfonate or is derived from some impurity in it.

Two experiments were made on silver salt, using crude in one case and recrystallized in the other, boiling 1 kg. of the salt for 4 hours with 8 liters of water, 40 g. of caustic soda and 80 g. of butyl mercaptan. The reaction mixture was filtered hot and the residue extracted with chloroform which was then evaporated leaving a red mass that appeared to be a thio-ether. In each case the amount of this was 13 g. No substance of constant properties has so far been isolated from this, or from the supposed sulfone obtained by oxidizing it with fuming nitric acid. Analyses indicate the presence of a monothio-ether, and melting points as well as mixed melting points show conclusively that little, if any, of the  $\alpha$ -thio-ether or its sulfone was present.

Dünschmann<sup>15</sup> separated some  $\alpha$ -sulfonic acid, by recrystallization of the sodium salts, from the products obtained by sulfonating anthraquinone in the usual way without catalyst. Liebermann and Pleus<sup>15</sup> showed that commercial "silver salt" contains some

<sup>14</sup> Preparation of compounds by A. T. Frascati; melting points and analyses by W. S. Hoffman.

<sup>15</sup> Liebermann and Pleus, *Ber.*, 37, 646 (1904).

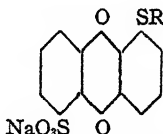
of the  $\alpha$ -salt but in neither case was any information obtained as to the proportion of the  $\alpha$ -salt except that its amount was small.

We sulfonated 208 g. of anthraquinone with oleum in the usual way and obtained 140 g. of silver salt (42.7%), and recovered 43.8% of the anthraquinone. The mercaptan reaction was tried as above with this silver salt and 1% of a thio-ether resembling that described above was obtained.

One-half of the mother liquor from which the silver salt separated was made alkaline and boiled with butyl mercaptan. The solution was filtered hot and the residue extracted with benzene which left 0.7 g. of a yellow thio-ether.

This melted at 89–92° and had the odor of butyl disulfide. It contained 11.64% of sulfur instead of 10.82% calculated for the butyl thio-ether. It was converted into the sulfone which melted at 150°; mixed with  $\alpha$ -sulfone (m. p. 150°) it melted also at 150°. It contained 9.86% sulfur as compared with calculated 9.77%. Thus it is proved that the mercaptan derivative obtained from the sulfonation mother liquor is the  $\alpha$ -thio-ether, confirming the presence of the  $\alpha$ -acid as a product of the sulfonation of anthraquinone without catalyst. For the total mother liquor 1.4 g. would have been obtained representing 1 g. of anthraquinone or about 1% of that sulfonated. As the mercaptan reaction is not quantitative but usually yields about 80%, we may say that something over 1% of the sulfonic acid groups enter the  $\alpha$ -position.

#### IV. Anthraquinone-1-alkyl-thio-ether-5-sulfonic Acid.



After several preliminary experiments with small quantities a mixture of 300 g. (or 0.61 mol.) of sodium anthraquinone-1,5-disulfonate ( $1,5\text{-C}_{14}\text{H}_8\text{O}_2(\text{SO}_3\text{Na})_2 \cdot 5\text{H}_2\text{O}$ ), 36 g. (or 0.9 mol.) of caustic soda, 120 g. (or 1.0 mol.) of butyl mercaptan (75%) and 4500 cc. of water, was boiled under a reflux condenser for 11 hours, cooled and filtered. The residue was washed with three 800cc. portions of water and dried. From 800 cc. of wash water 1 g. of the barium salt was obtained by precipitation with barium chloride, showing that the sodium salt is soluble in about 1000 parts of cold water. The residue was extracted thrice with hot benzene which removed about 4 g. of the 1,5-anthraquinone-dibutyl-dithio-ether. Hence the yield is 95% of the calculated, while the dithio-ether formed amounts to only 1.6%.

As the monothio-ether-sulfonate, the first reaction product, is only slightly soluble even in hot water, its effective concentration is not enough to push the second reaction. Using ethyl mercaptan where the intermediate product is more soluble about 10% of the dithio-ether was obtained.

The anthraquinone-1-butyl-thio-ether sodium sulfonate obtained as above is a beautiful golden-yellow, with only a slight reddish tinge, closely resembling mosaic gold and we have called it the "gold salt" to correspond with the "silver salt" which is sodium  $\beta$ -anthraquinone sulfonate. Both of these salts lose their metallic sheen when recrystallized. The "gold salt" then appears as glittering orange-red needles.

This salt in a 2% bath dyes<sup>16</sup> unmordanted wool a slightly orange-yellow. It is a bright attractive color and is fairly fast to light but not fast to washing and milling. The bath is exhausted by the wool. The tinctorial power is not sufficient for a valuable dye. With chromium as a mordant, wool is dyed a greenish-yellow. The corresponding ethyl derivative dyes unmordanted wool a pure yellow.

<sup>16</sup> Experiments in the Dye Laboratory of E. I. du Pont de Nemours and Co.

If various metallic salts are added to the bath in which wool is being dyed with the sodium salt, various widely different colors may be obtained; thus a barium salt gives a red and a lead salt a chocolate-brown.

Although the butyl-thio-ether sodium sulfonate is only slightly soluble in hot water it is soluble enough so that other salts, particularly those of the heavy metals and of the aromatic amines, can be prepared from it by double decomposition. For this purpose the sodium salt is dissolved in boiling water and an equivalent amount of a neutral solution of some soluble salt of the desired base is added. The most of these salts are too insoluble to be recrystallized but soluble impurities can be removed by extraction with boiling water. Many such salts containing various alkyls have been thus prepared. The salts are lustrous and many of them highly colored.

The corresponding derivatives with other mercaptans were not so extensively studied. The details of these preparations of the sodium salts are given in tabular form. All of these salts contain one molecule of water.

TABLE IV.

PREPARATION OF ANTHRAQUINONE-1-ALKYL-THIO-ETHER-5-SODIUM SULFONATES.  
1,5-RS.C<sub>14</sub>H<sub>9</sub>O<sub>2</sub>.SO<sub>3</sub>Na.H<sub>2</sub>O.

Alkyl.	Sulfonate G.	Water. Cc.	NaOH. G.	RSH.	Time. Hrs.	Yield. G.	%.
Methyl	50	400	13	gas	2	30	65
Ethyl	100	600	26	gas	1	38	42
Propyl	50	1000	10	12	1	23	50
Butyl	50	500	16	15	7	30	62
<i>iso</i> -Amyl	100	1000	32	34	15	55	55

TABLE V.

ANALYSES AND PROPERTIES OF SODIUM SALTS. 1,5-RS.C<sub>14</sub>H<sub>9</sub>O<sub>2</sub>.SO<sub>3</sub>Na.H<sub>2</sub>O.

Alkyl.	Water.		Sodium.		Color and form.
	Calc. %.	Found. %.	Calc. %.	Found. %.	
Methyl	4.81	4.86	6.46	6.27	orange-red needles
Ethyl	4.64	4.93	6.21	6.04	dark orange-red needles
Propyl	4.48	4.42	5.98	5.92	rich orange-red needles
Butyl	4.33	4.41	5.77	5.77	orange-red needles
<i>iso</i> -Amyl	4.19	4.26	5.58	5.43	orange-red needles

*Barium, Calcium and Strontium Salts.*—These were made by dissolving the sodium salts in hot water and adding the calculated amounts of the chlorides of the other metals. The resulting salts are extremely insoluble and are purified by boiling out with water.

TABLE VI.

BARIUM SALTS. 1,5-(RS.C<sub>14</sub>H<sub>9</sub>O<sub>2</sub>SO<sub>3</sub>)<sub>2</sub>Ba.

Alkyl.	Barium.		Color and form.
	Calc. %.	Found. %.	
Methyl	17.09	17.00	red needles
Ethyl	16.51	16.50	red crystal powder
Propyl	15.97	15.58	orange-red needles
Butyl	15.47	15.43	red crystals
<i>iso</i> -Amyl	14.99	14.56	red crystals

The strontium and calcium salts also were made of the butyl acid, the strontium salt being anhydrous, (Sr, calc. 10.45; found, 10.40). The calcium salt, unlike the others contains 4 molecules of water of crystallization, showing by analysis 8.12%

of water and 5.09% of calcium compared to 8.35 and 5.07% respectively, by formula. The barium salt is a deep red and the calcium salt an orange-red, while the strontium salt is intermediate.

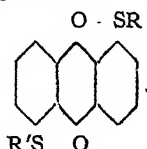
*Aniline, o- and p-Toluidine Salts.*—These salts were made by adding the corresponding hydrochlorides to the hot, saturated solutions of the sodium salts. All of them are very insoluble and precipitate. They were purified by extraction with hot water. They all separate as fine yellow needles which melt with decomposition at from 250° to 300°. These temperatures are not sharp enough for characterization as had been hoped. The *o*-toluidine salts decompose at lower temperatures than the aniline or *p*-toluidine.

TABLE VII.

ANILINE, *o*-TOLUIDINE AND *p*-TOLUIDINE SALTS. 1,5-RS.C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>.SO<sub>3</sub>H<sub>2</sub>NAr.

Alkyl.	Base.	Decomp. temp. °C.	Sulfur.	
			Calc. %.	Found. %.
Methyl	Aniline	290–299	15.00	14.70
	<i>o</i> -Toluidine	285–290	14.53	14.75
	<i>p</i> -Toluidine	298–304	14.53	14.50
Ethyl	Aniline	276–285	14.53	14.30
	<i>o</i> -Toluidine	264–274	14.08	14.10
	<i>p</i> -Toluidine	276–285	14.08	14.25
Propyl	Aniline	270–277	14.08	14.15
	<i>o</i> -Toluidine	255–257	13.66	13.75
	<i>p</i> -Toluidine	.....	13.66	13.85
Butyl	Aniline	257–259	13.66	13.80
	<i>o</i> -Toluidine	234–237	13.26	13.35
	<i>p</i> -Toluidine	256–260	13.26	13.10
<i>iso</i> -Amyl	Aniline	263–265	13.26	13.10
	<i>o</i> -Toluidine	250–254	12.89	12.80
	<i>p</i> -Toluidine	267–277	12.89	12.90

## V. 1,5-Anthraquinone Dialkyl Dithio-ethers.



When the two alkyl groups are the same, these may be obtained directly by heating the sodium 1,5-disulfonate with excess of alkali and mercaptan for a long time. They are always formed to a greater or less extent in the preparation of the intermediate thio-ether sulfonates described above and are obtained by extraction of the crude products with benzene. The diethyl and dibutyl compounds were obtained in this way.

The intermediate monosulfonate may be isolated and purified and the second alkyl group, which may be the same as the first or different, introduced. Of course the mixed thio-ethers must be prepared in this way.

The alkyl thio-ether sodium sulfonate is suspended in about 100 parts of water, containing an excess of caustic soda with the mercaptan, and the mixture boiled. The reaction is slow on account of the low solubility of the sodium salts, particularly of those containing the higher alkyl groups. It is best to introduce the lower alkyl group first. The resulting dithio-ethers are extracted with hot benzene and recrystallized from benzene, or alcohol, or mixtures of the two. The details of the various preparations are given in tabular form.



TABLE VIII.

PREPARATION OF 1,5-ANTHRAQUINONE				DIALKYL DITHIO-ETHERS.			
First alkyl.	Alkyl introduced.	Wt. sulfonate. G.	Vol. water. Cc.	Caustic soda. G.	Wt. RSH. G.	Time. Hours.	Yield. G.
Methyl	Methyl	5	500	2	gas	4	4
	Ethyl	10	500	4	gas	4	1
	Propyl	8	500	2	6	23	5
	Butyl	8	500	2	4.6	22	5
	<i>iso</i> -Amyl	8	500	2	4.4	6	6
Ethyl	Propyl	5	350	2	5	30	4
	Butyl	5	350	2	5	30	4
	<i>iso</i> -Amyl	5	300	2	5	12	4.5
Propyl	Propyl	10	750	2	6	20	7
	Butyl	8	750	2	6	7	3
<i>iso</i> -Amyl	Butyl	10	1000	2	5	41	6.5
	<i>iso</i> -Amyl	10	300	2	5	11	2.5

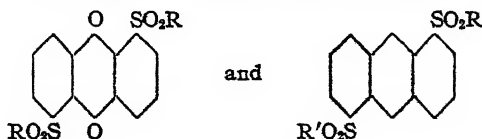
TABLE IX.

PROPERTIES AND ANALYSES OF 1,5-ANTHRAQUINONE DIALKYL DITHIO-ETHERS. 1,5- $C_{14}H_6O_2(SR)_2$  AND 1,5-RS. $C_{14}H_6O_2$ .SR'.

Alkyls.		Sulfur.			Color and form.
		M. p. °C.	Calc. %.	Found. %.	
Methyl	Methyl	Chars.	21.35	21.03	red needles
	Ethyl	229	20.40	20.35	yellow needles
	Propyl	209	19.53	19.45	orange needles
	Butyl	173.5	18.73	18.50	yellow needles
	<i>iso</i> -Amyl	175	17.99	17.90	orange-yel. leaflets
Ethyl	Ethyl	226.5	19.53	19.40	orange grains
	Propyl	188.5	18.73	18.65	orange grains
	Butyl	156	17.99	17.75	red crystals
	<i>iso</i> -Amyl	152	17.31	17.25	gold-yellow plates
Propyl	Propyl	227	17.99	18.30	orange cryst. powder
	Butyl	175	17.31	16.95	orange prisms
Butyl	Butyl	159.5	16.68	16.65	yellow needles
	<i>iso</i> -Amyl	134	16.09	15.80	orange needles
Di- <i>iso</i> -amyl		158.5	15.55	15.59	yellow needles

Comparing these, we see that the dimethyl compound has the highest melting point and that the melting point is progressively lowered as heavier alkyl groups are substituted for one of the methyls. Gattermann gives the diethyl thio-ether as melting at 230°.

#### VI. 1,5-Anthraquinone Dialkyl Disulfones.



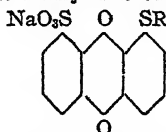
These were prepared just as were the monosulfones by oxidizing the dithio-ethers with fuming nitric acid. They separate as faintly yellow crystalline powders, when their nitric acid solutions are poured into hot water. They are very slightly soluble in most solvents.

TABLE X.

PROPERTIES AND ANALYSES OF 1,5-ANTHRAQUINONE DIALKYL DISULFONES,  $1,5\text{-C}_{14}\text{H}_6\text{O}_2\text{-(SO}_2\text{R)}_2$  AND  $1,5\text{-R'SO}_2\text{C}_{14}\text{H}_6\text{O}_2\text{SO}_2\text{R}$ .

Alkyls.		M. p.	Sulfur.		Form.
		° C.	Calc.	Found.	
		chars.	%. Found.	%.	
Methyl	Methyl	>300	17.60	17.53	powder
	Ethyl	291	16.95	16.90	fine needles
	Propyl	264	16.34	16.50	crystalline grains
	Butyl	266	15.78	15.75	crystalline grains
	<i>iso</i> -Amyl	269.5	15.25	15.00	crystalline grains
Ethyl	Ethyl	243.5	16.34	16.40	fine needles
	Propyl	194	15.78	15.65	fine needles
	Butyl	198	15.25	15.45	powder
	<i>iso</i> -Amyl	265	14.76	14.80	powder
Propyl	Propyl	220	15.25	15.15	fine needles
	Butyl	184.5	14.76	14.95	crystalline grains
Butyl	Butyl	203.5	14.30	14.10	crystalline powder
	<i>iso</i> -Amyl	202	13.87	14.00	crystalline powder
<i>iso</i> -Amyl	<i>iso</i> -Amyl	13.46	13.50		powder

## VII. Anthraquinone-1-alkyl-thio-ether-8-sulfonic Acids.



These can be prepared just as the corresponding 1,5 compounds except that it is much more difficult to isolate the sodium salts as, on account of their greater solubility, they react readily with a second molecule of the mercaptan to give the disulfides. In an experiment in which 50 g. of sodium anthraquinone-1-8-disulfonate, 800 cc. of water, 13 g. of caustic soda and 37 g. of butyl mercaptan were heated for 24 hours at 100°, 20 g. or 55% of the dithio-ether was formed.

The details of a number of preparations are given in tabular form.

TABLE XI.

PREPARATION OF SODIUM ANTHRAQUINONE-1-ALKYL-THIO-ETHER-8-SULFONATES.

1,8-RS.C <sub>14</sub> H <sub>6</sub> O <sub>2</sub> .SO <sub>2</sub> Na.H <sub>2</sub> O.						
Alkyl.	Sulfonate. G.	Water. Cc.	NaOH. G.	RSH. G.	Time. Hrs.	Yield. %.
Methyl	82	500	25	gas	2	57
Ethyl	82	500	25	gas	3	45
Propyl	82	500	8	36	3	21
Butyl	82	500	8	24	2	30
<i>iso</i> -Amyl	82	500	10	28	4	50

TABLE XII.

PROPERTIES AND ANALYSES OF SODIUM SALTS.  $1,8\text{-RS.C}_{14}\text{H}_6\text{O}_2\text{SO}_2\text{Na.H}_2\text{O}$ .

Alkyl.	Water.		Sodium.		Color and form.
	Calc. %.	Found. %.	Calc. %.	Found. %.	
Methyl	4.81	4.84	6.45	6.60	brick-red cryst.
Ethyl	..	..	6.21	6.11	orange needles
Propyl	2.29	2.26	5.98	6.23	ochre-yellow, m. p. 289°
Butyl	4.33	4.39	5.77	5.59	orange-yellow needles
<i>iso</i> -Amyl	4.19	4.16	5.58	5.34	brownish-orange needles

The ethyl compound is anhydrous and the propyl contains only one-half molecule of water.

TABLE XIII.

PROPERTIES AND ANALYSES OF BARIUM SALTS.  $1,8-(RSC_{14}H_9O_2SO_3)_2Ba$ .

Alkyl.	Barium.		Color and form.
	Calc. %.	Found. %.	
Methyl	17.09	16.73	brick-red cryst. powder
Ethyl	16.51	16.31	orange needles
Propyl	15.97	16.08	orange powder
Butyl	15.47	15.12	orange needles
iso-Amyl	14.99	14.80	brownish-orange needles

TABLE XIV.

OTHER SALTS OF ANTHRAQUINONE-1-BUTYL-THIO-ETHER-8-SULFONIC ACID.  $1,8-(C_4H_9SC_{14}H_9O_2SO_3)_2M'$ .

Base.	Water of hydration.	Water.		Metal.		Color and form.
		Calc. %.	Found. %.	Calc. %.	Found. %.	
Strontium	...	..	..	10.45	10.63	orange-red powder
Calcium	4 H <sub>2</sub> O	8.35	7.87	5.07	5.10	red cryst. powder
Lead	...	..	..	21.63	21.69	orange-red powder
Nickel	$x$ H <sub>2</sub> O	..	..	7.25	7.08	orange-red needles
Cobalt	$x$ H <sub>2</sub> O	..	..	7.28	7.40	orange-red needles
Copper	3 H <sub>2</sub> O	3.21	3.40	7.81	7.85	ochre-yellow needles

The nickel and cobalt salts contain water, but it was not determined.

The sodium butyl compound dyes unmordanted wool much as does the corresponding 1,5 salt but the shades obtained were dull and unattractive.

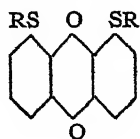
*Aniline, o- and p-Toluidine Salts.*—These were made by precipitation as in the other series. All of them come down as fine needles with colors varying from yellow to orange.

TABLE XV.

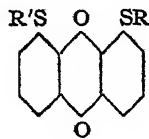
ANILINE, o-TOLUIDINE AND p-TOLUIDINE SALTS.  $1,8-RS.C_{14}H_9O_2.SO_3H_2NaR$ .

Alkyl.	Base.	Decomp. Temp. °C.	Sulfur.		Color.
			Calc. %.	Found. %.	
Methyl	Aniline	260	15.00	14.85	orange
	o-Toluidine	255	14.53	14.30	yellow
	p-Toluidine	260	14.53	14.37	orange
Ethyl	Aniline	250	14.08	14.01	orange
	o-Toluidine	260	13.66	13.64	yellow
	p-Toluidine	255	13.66	13.56	orange
Propyl	Aniline	242	13.66	13.85	yellow
	o-Toluidine	260	13.26	13.60	yellow
	p-Toluidine	260	13.26	13.50	yellow
Butyl	Aniline	260	13.26	13.47	orange
	o-Toluidine	260	12.89	13.06	orange
	p-Toluidine	255	12.89	12.98	orange

## VIII. 1,8-Anthraquinone Dialkyl Dithio-ethers.



and



The compounds in which the two alkyls are the same are readily obtained directly from the sodium 1,8-disulfonate. Those described below were obtained in this way as by-products in the preparation of the monosulfonates described above. The mixed compounds were prepared as were the corresponding 1,5 compounds. The details are given in tabular form.

TABLE XVI.

PREPARATION OF 1,8-ANTHRAQUINONE DIALKYL DITHIO-ETHERS.							
Original alkyl.	Alkyl introduced.	Sulfonate. G.	Water. Cc.	NaOH. G.	RSH. G.	Time. Hours.	Yield. G.
Methyl	Ethyl	6	300	1	gas	3	3.5
	Propyl	6	300	1	2	3	5
	Butyl	6	250	1	2	3	4
	<i>iso</i> -Amyl	7	200	1	2	3	3.5
Propyl	<i>iso</i> -Amyl	7	250	1	2	4	4
Butyl	Ethyl	10	50	1	5	3	3
	Propyl	5	50	1	2	6	5
	<i>iso</i> -Amyl	7	250	1	2	3	4
	<i>iso</i> -Amyl	7	300	1	2	3	4

TABLE XVII.

PROPERTIES AND ANALYSES OF 1,8-ANTHRAQUINONE DIALKYL DITHIO-ETHERS.  
1,8-C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>(SR)<sub>2</sub> AND 1,8-R'S.C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>.SR.

Alkyl.		M. p. °C.	Calc. %.	Sulfur. Found. %.	Color and form.
Methyl	Methyl	222	21.35	21.11	brownish-yellow needles
	Ethyl	210	20.40	20.45	red crystals
	Propyl	173.5	19.53	19.60	orange-red needles
	Butyl	134	18.73	18.74	orange needles
	<i>iso</i> -Amyl	114	17.99	18.10	fine orange needles
Ethyl	Ethyl	167.5	19.53	19.44	red crystals
	Butyl	95	17.99	18.14	orange-yellow needles
Propyl	Propyl	142	17.99	17.87	brick-red prisms
	Butyl	119.5	17.31	17.20	orange needles
	<i>iso</i> -Amyl	104	16.68	16.58	orange powder
Butyl	Butyl	131	16.68	16.67	red needles
	<i>iso</i> -Butyl	103.5	16.68	16.70	orange prisms
	<i>iso</i> -Amyl	116.5	16.09	16.21	orange crystals
Di- <i>iso</i> -amyl		133	15.55	15.27	long orange plates

## IX. 1,8-Anthraquinone Dialkyl Disulfones.

1,8-R'SO<sub>2</sub>.C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>.SO<sub>2</sub>R.

These sulfones are readily obtained by oxidation of the thio-ethers with fuming nitric acid. They are all very slightly yellow crystalline powders.

TABLE XVIII.

PROPERTIES AND ANALYSES OF 1,8-ANTHRAQUINONE DIALKYL DISULFONES.  
1,8-C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>(SO<sub>2</sub>R)<sub>2</sub> AND 1,8-R'SO<sub>2</sub>.C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>.SO<sub>2</sub>R.

Alkyl.		M. p. °C.	Calc. %.	Sulfur. Found. %.
Methyl	Methyl	310	17.60	17.35
	Ethyl	220	16.95	16.79
	Propyl	211	16.34	16.38

TABLE VIII (continued).

Alkyl.		M. p. ° C.	Calc. %.	Sulfur. Found. %.
	Butyl	169	15.78	15.38
	<i>iso</i> -Amyl	172	15.25	15.09
Ethyl	Ethyl	228	16.34	16.26
	Butyl	128	15.25	15.45
Propyl	Propyl	210	15.25	14.80
	Butyl	200.5	14.76	14.70
	<i>iso</i> -Amyl	147.5	14.30	13.95
Butyl	Butyl	138	14.30	14.00
	<i>iso</i> -Butyl	168.5	14.30	13.95
	<i>iso</i> -Amyl	154	13.87	13.94
Di- <i>iso</i> -amyl		176	13.46	13.40

## Summary.

It has been found that by heating the sodium salt of  $\alpha$ -anthraquinone sulfonic acid with a mercaptan in presence of caustic soda, the sulfonic acid group is readily replaced yielding an anthraquinone alkyl thio-ether,  $C_{14}H_7O_2SR$ . When two  $\alpha$ -sulfonic acid groups are present these are replaced in succession, yielding first alkyl thio-ether sulfonic acids, 1,5- and 1,8- $NaO_3S.C_{14}H_6O_2.SR$  and then dialkyl dithio-ethers, 1,5- and 1,8- $R'S.C_{14}H_6O_2.SR$ . A large number of compounds have been prepared in which R is methyl, ethyl, propyl, butyl, *isobutyl* and *iso*-amyl.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS,  
NORTHWESTERN UNIVERSITY.]

ARSENATED BENZOPHENONE AND ITS DERIVATIVES.<sup>1</sup>

BY W. LEE LEWIS AND H. C. CHEETHAM.

Received June 11, 1921.

## Introduction.

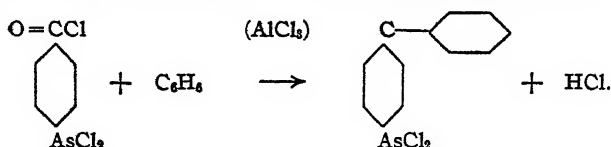
Arsenic in an aromatic nucleus does not interfere with many typical organic reactions. The Friedel and Crafts reaction, however, has found but limited<sup>2</sup> application in organic arsenical chemistry. With a view to determining whether arsenated benzoyl chloride would enter into the Friedel and Crafts reaction, thus yielding a new type of arsenic compound of possible therapeutic value,<sup>3</sup> the work described in this paper was undertaken.

<sup>1</sup> This work was done under a grant from the Interdepartmental Hygiene Board, Washington, D. C., Dr. T. A. Storey, Sec'y.

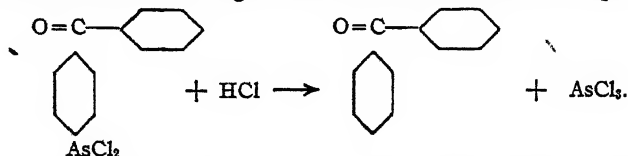
<sup>2</sup> Lewis, Lowry and Bergeim, *THIS JOURNAL*, 43, 892 (1921).

<sup>3</sup> Therapeutic tests upon new compounds developed under this grant are being conducted by Dr. A. S. Loevenhart, Department of Pharmacology, University of Wisconsin.

It has been found that dichloro-*p*-arsinobenzoyl chloride condenses quite readily with aromatic hydrocarbons and phenyl ethers in the presence of anhydrous aluminum chloride using carbon disulfide as a solvent. When benzene was coupled with the arsenated acid chloride, some benzophenone itself was found among the products of the reaction, and identified by conversion into its oxime, melting at 140°. The formation of benzophenone establishes the course of the main reaction as follows.



When the reaction is too vigorous, de-arsenation of the compound results.



The amount of benzophenone never exceeded 10%, usually running 0.5–1%, while the yield of arsenated benzophenone was 50–60%. That the arsenated product is a ketone is shown by the fact that it reacts with hydroxylamine to form an oxime of the formula  $\text{C}_6\text{H}_5\text{C}(\text{NOH})\text{C}_6\text{H}_4\text{AsO}_3\text{H}_2$ . Furthermore, de-arsenation of the pure product by long refluxing with conc. hydrochloric acid yields benzophenone.

### Experimental.

**Preparation of Benzarsonic Acid.**—Since a considerable quantity of benzarsonic acid (*p*-carboxy-phenylarsonic acid) was required for this work, a comparative study was made of the available methods of preparation. Of the three processes described in the literature, the first involves the oxidation of *p*-tolylarsonic acid by means of alkaline potassium permanganate.<sup>4</sup> The yield is about 60% of the calculated amount, but the process is slow and tedious. A second method uses dil. nitric acid<sup>5</sup> in sealed tubes in the oxidation of *p*-tolylarsonic acid. The yield is practically quantitative, but working in sealed tubes at 150° limits the amount of material, and the high pressure developed breaks a large percentage of the tubes. In the third process, arsanilic acid is diazotized,<sup>6</sup> the cyanogen group introduced through the Sandmeyer reaction, and hydrolyzed to benzarsonic acid. The yield is uncertain and the method expensive.

A more economical and time-saving method was developed as follows. *p*-Nitrobenzoic acid is reduced to *p*-aminobenzoic acid, which is converted to the corresponding arsonic acid by Bart's reaction.<sup>7</sup>

**Reduction of *p*-Nitrobenzoic Acid.**—The method of Jacobs and Heidelberg<sup>8</sup> was

<sup>4</sup> La Coste, *Ann.*, 208, 1 (1881).

<sup>5</sup> Michaelis, *ibid.*, 320, 303 (1902); *Ber.*, 48, 870 (1915).

<sup>6</sup> Bertheim, *Ber.*, 41, 1857 (1908).

<sup>7</sup> Bart, *Ger. pat.* 250,264 and 254,345.

<sup>8</sup> Jacobs and Heidelberg, *THIS JOURNAL*, 39, 1437 (1917).

applied with excellent results in this reduction. Twenty-five g. of *p*-nitro-benzoic acid (technical) is dissolved in a small amount of warm dil. ammonium hydroxide and poured with stirring into a boiling solution of 300 g. of commercial ferrous sulfate crystals in 400 cc. of water. About 100 cc. of conc. ammonium hydroxide is cautiously added, and the boiling continued for 5 minutes. The product is filtered hot after the addition of 50 cc. of ammonium hydroxide. On acidifying the filtrate with acetic acid, *p*-amino-benzoic acid crystallizes in long, light yellow needles; m. p., 186°; yield, 85-90%.

**Conversion of *p*-Aminobenzoic Acid to Benzarsonic Acid.**—The method of Bart is applied as follows. Fifty g. of *p*-aminobenzoic acid is dissolved in 750 cc. of water with 75 cc. of conc. hydrochloric acid and diazotized in the usual manner, using 26 g. of sodium nitrite. The arsenite solution is prepared by dissolving 46 g. of arsenic trioxide in 400 cc. of water with 54 g. of sodium hydroxide. Twenty cc. of 6 *N* copper sulfate solution is now added. The diazo solution is slowly poured into the arsenite-solution with vigorous stirring, the temperature being held at 20°. The alkaline solution is then warmed on the water-bath to 60° until the evolution of nitrogen ceases, when it is acidified with hydrochloric acid. A water-insoluble flocculent precipitate is filtered and discarded. The filtrate on concentrating to 500 cc., cooling, and scratching, deposits colorless crystals of benzarsonic acid. The yield is 50-60%.

**Preparation of Dichloro-*p*-arsinobenzoyl Chloride,**  $\text{Cl}_2\text{AsC}_6\text{H}_4\text{COCl}$ .—Twenty cc. of phosphorus trichloride in 20 cc. of chloroform is slowly added to 25 g. of benzarsonic acid suspended in 100 cc. of cold chloroform. After warming to complete the reaction, 20 g. of phosphorus pentachloride is added at once. When this second reaction has been completed by heating the solution on a water-bath for 10 to 15 minutes, the mixture is fractionated *in vacuo*. Dichloro-*p*-arsino-benzoyl chloride passes over at 190-195° under 20-25 mm. pressure. The yield is 75-80%. In later runs with larger amounts the fractionation was omitted, the material being used directly for the condensation with aluminum chloride.

**Preparation of Benzophenone-*p*-arsenious Oxide,**  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_4\text{As}=\text{O}$ .—Twenty g. of the above acid chloride, dissolved in 100 cc. of dry carbon disulfide, is added to 25 cc. of dry benzene. Twenty-five g. of anhydrous aluminum chloride is then added in 5g. portions to reduce the intensity of the reaction. After warming at 50° on the water-bath for 2 hours under a reflux condenser, the reaction mixture is poured while warm on 300 g. of cracked ice. Ten cc. of conc. hydrochloric acid is added, and the carbon disulfide and excess benzene removed by steam distillation. The reaction flask now contains a clear aqueous solution and a gummy substance which adheres to the walls of the flask. The aqueous solution, which contains the hydrated aluminum chloride and some *p*-carboxy-phenylarsenious acid is decanted and discarded. Four hundred cc. of dil. sodium carbonate solution and 50 cc. of 6 *N* sodium hydroxide solution are added to the flask and warmed to decompose the gummy mass which gradually goes into solution. After filtering and cooling, benzophenone-*p*-arsenious oxide is precipitated in an amorphous condition by dil. hydrochloric acid. The yield is 60%. It is slightly soluble in boiling water, absolute alcohol, benzene, and ether, and easily soluble in warm alkalis.

*Analyses.* Subs., 0.2442, 0.1643: 34.5 cc., 23.3 cc. of 0.0521 *N* iodine solution. Calc. for  $\text{C}_{13}\text{H}_9\text{O}_2\text{As}$ : As, 27.57. Found: 27.59, 27.69.

**Benzophenone-*p*-arsenious Acid,**  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_4\text{As}(\text{OH})_2$ .—The above oxide, after boiling for several hours with a large amount of water, yields a small quantity of fine crystals insoluble in ether or benzene, easily soluble in cold alkalis, and somewhat soluble in absolute alcohol. It is apparently the hydrated oxide.

<sup>9</sup> Poulenc, French pat. 441,215.

*Analyses.* Subs., 0.2681: 46.95 cc. of 0.0389 *N* iodine solution. Calc. for  $C_{13}H_{11}O_2As$ : As, 25.86. Found: 25.57.

**Benzophenone-*p*-arsonic Acid**,  $C_6H_5COC_6H_4AsO_3H_2$ .—The oxide is dissolved in warm dil. sodium hydroxide and a slight excess of the calculated amount of 3% hydrogen peroxide solution added. After warming for 5 minutes, the solution is acidified with hydrochloric acid, which precipitates at once the arsonic acid. From large volumes of boiling water, recrystallization yields lustrous clusters of elongated plates. The yield is quantitative. The crystals soften at 195° but do not melt below 260°. The substance is insoluble in cold water, benzene, and ether, and soluble in alkalis, ethyl alcohol, and warm glacial acetic acid.

*Analyses.* Subs., 0.2214, 0.1579: 27.8 cc., 19.7 cc. of 0.0521 *N* iodine solution. Calc. for  $C_{13}H_{11}O_4As$ : As, 24.51. Found: 24.52, 24.35.

**Oxime of Benzophenone-*p*-arsonic Acid**,  $C_6H_5C(=NOH)C_6H_4AsO_3H_2$ .—Ten g. of benzophenone-*p*-arsonic acid is heated in a slightly alkaline alcoholic solution with 5 g. of hydroxylamine sulfate on the water-bath for 2 hours. After cooling and acidifying with dil. sulfuric acid, the product is recrystallized from hot water, yielding fine colorless needles which do not melt below 260°. The yield is 80%.

*Analyses.* Subs., 0.4611: 12.8 cc. of 0.108 *N* sodium hydroxide (Kjeldahl). Calc. for  $C_{14}H_{13}O_4NAs$ : N, 4.36. Found: 4.20.

Subs., 0.1390: 17.15 cc. of 0.0497 *N* iodine solution. Calc. for  $C_{13}H_{12}O_4NAs$ : As, 23.36. Found: 23.01.

**Mononitro-benzophenone-*p*-arsonic Acid**,  $(NO_2)C_6H_4COC_6H_4AsO_3H_2$ .—Thirty-five g. of fuming nitric acid (sp. gr. 1.5) is added to 4 g. of benzophenone-*p*-arsonic acid and the solution heated on the water-bath for one hour. After dilution with 50 cc. of water, the mixture is slowly evaporated to a thick syrup to expel the nitrous fumes. After two recrystallizations from hot water, 2 g. of fine, light yellow needles were obtained.

*Analyses.* Subs., 0.5385: 12.95 cc. of 0.108 *N* sodium hydroxide (Kjeldahl). Calc. for  $C_{12}H_{10}O_6NAs$ : N, 3.98. Found: 3.65.

Subs., 0.3719: 40.45 cc. of 0.0521 *N* iodine solution. Calc. for  $C_{13}H_{10}O_6NAs$ : As, 21.36. Found: 21.24.

**4-Methyl-benzophenone-4'-arsenious Oxide**,  $CH_3C_6H_4COC_6H_4AsO$ .—This compound is made by substituting toluene for benzene in the procedure described above for benzophenone-*p*-arsenious oxide. The yield is about 50%. Due to its amorphous character, the product is difficult to purify, and arsenic analyses give results 0.5–0.7% low. Its hydrate is made by prolonged boiling with a large volume of water, giving a small quantity of fine, needle-like crystals, soluble in alkalis, insoluble in ether, or benzene, and somewhat soluble in ethyl alcohol.

*Analyses.* Subs., 0.2658, 0.1904: 22.5 cc., 16.05 cc. of 0.0772 *N* iodine solution. Calc. for  $C_{14}H_{13}O_2As$ : As, 24.67. Found: 24.50, 24.40.

**4-Methyl-benzophenone-4'-arsonic Acid**,  $CH_3C_6H_4COC_6H_4AsO_3H_2$ .—Oxidation of the above oxide in warm alkaline solution by means of 3% hydrogen peroxide gives a good yield of the corresponding arsonic acid, which crystallizes from hot water in transparent plates, easily soluble in alkalis, somewhat soluble in ethyl alcohol, insoluble in ether, benzene, etc. The crystals did not melt below 260°.

*Analysis.* Subs., 0.1330: 15.9 cc. of 0.0521 *N* iodine solution. Calc. for  $C_{14}H_{13}O_4As$ : As, 23.43. Found: 23.34.

The condensation of dichloro-*p*-arsinobenzoyl chloride with the phenyl ethers proceeds very smoothly, giving 60–75% yields. In each case the substituted arsenious oxides were found to be amorphous and difficult to purify, and they yielded no



crystalline hydrates. They were therefore oxidized to the corresponding arsonic acids, which are well crystallized and easily purified.

**4-Methoxy-benzophenone-4'-arsonic Acid**,  $\text{CH}_3\text{OC}_6\text{H}_4\text{COC}_6\text{H}_4\text{AsO}_3\text{H}_2$ .—Starting with anisole in place of benzene in the original condensation and oxidizing the intermediate arsine oxide without attempting to isolate it, the corresponding arsonic acid is obtained in 60–70% yield after recrystallization from large volumes of boiling water.

*Analysis.* Subs., 0.3319: 37.4 cc. of 0.0521 *N* iodine solution. Calc. for  $\text{C}_{14}\text{H}_{13}\text{O}_5\text{As}$ : As, 22.32. Found: 22.01.

**4-Ethoxy-benzophenone-4'-arsonic Acid**,  $\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{COC}_6\text{H}_4\text{AsO}_3\text{H}_2$ .—Following the same procedure, phenetole gives a 55% yield of the ethoxy-derivative. As the molecular weight increases, the solubility of these arsonic acids in water decreases, so that it becomes difficult to use water as a solvent for recrystallization. Glacial acetic acid or 95% ethyl alcohol is found satisfactory.

*Analysis.* Subs., 0.2193: 24.95 cc. of 0.0497 *N* iodine solution. Calc. for  $\text{C}_{18}\text{H}_{18}\text{O}_5\text{As}$ : As, 21.42. Found: 21.21.

**4-Phenoxy-benzophenone-4'-arsonic Acid**,  $\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{COC}_6\text{H}_4\text{AsO}_3\text{H}_2$ .—This arsonic acid is made in 50% yield by using diphenyl ether. It is practically insoluble in water, even at 100°. It is easily crystallized from hot glacial acetic acid or 95% alcohol, giving colorless platelets, which do not melt below 260°.

*Analyses.* Subs., 0.1745: 16.7 cc. of 0.0521 *N* iodine solution. Calc. for  $\text{C}_{19}\text{H}_{15}\text{O}_5\text{As}$ : As, 18.84. Found: 18.69.

Similar compounds have been made from the *ortho* and *meta* homologs of dichloro-*p*-arsinobenzoyl chloride, and will be reported later.

### Summary.

1. It has been found possible to condense dichloro-*p*-arsinobenzoyl chloride with benzene, toluene, anisole, phenetole, and diphenyl ether in the presence of aluminum trichloride with carbon disulfide as a solvent.

2. Properties and directions for preparing the following compounds are given: benzophenone-*p*-arsenious oxide, benzophenone-*p*-arsenious acid, benzophenone-*p*-arsonic acid and its oxime and mononitro derivative, 4-methyl-benzophenone-4'-arsenic acid, 4-methoxy-benzophenone-4'-arsonic acid, 4-ethoxy-benzophenone-4'-arsonic acid, and 4-phenoxy-benzophenone-4'-arsonic acid.

3. An improved method for the preparation of benzarsonic acid has been developed.

EVANSTON, ILLINOIS.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

**C<sub>18</sub> FATTY ACIDS. II. THE RELATION OF OLEIC AND ELAIDIC ACIDS TO THEIR HALOGEN ADDITION PRODUCTS.**

BY BEN H. NICOLET.

Received June 20, 1921.

One of the most interesting problems in the chemistry of vegetable oils, is the question of the exact constitution of the linolic acids which they contain. Assuming, as is not improbable, that in most<sup>1</sup> oils the acids of the formula  $C_{18}H_{32}O_2$  have their double bonds in the same position, there are nevertheless 4 possible space-isomers (*cis-trans*), and at least two, or perhaps more, of these seem to occur mixed together in each of the commoner oils.<sup>2</sup>

Although at least 2 tetrabromo-stearic acids, and probably 2 tetrahydroxy-stearic acids, have been obtained as derivatives of ordinary "linolic" acid, there is at present no evidence known to the writer which relates a particular tetrabromo acid to a particular tetrahydroxy acid, or which indicates definitely the spatial structure of any one of these derivatives. Takahashi<sup>3</sup> has shown that each of the known tetrabromo acids, when reconverted into linolic acid and again brominated, gives a *mixture* of tetrabromo-stearic acids, in substantially the same proportions as are obtained in brominating the fatty acids of the common oils containing linolic acid. It is therefore evident that a rearrangement has taken place, either in the removal of the bromine to regenerate the double bonds, or in the subsequent addition of bromine to the products thus obtained. Incidentally, as this is the only known method of preparing substantially pure "linolic" acid, it becomes doubtful whether anyone has ever prepared this substance in a form which was not a mixture of at least two, and perhaps more, of the possible isomers.

The present paper describes an attempt, which was unsuccessful, to decide whether this rearrangement took place in the removal, or in the addition of bromine. As there is at present no good method of identifying linolic acid except by the preparation of saturated derivatives,<sup>3</sup> the elimination of bromine from dibromo-oleic and -elaidic acids and its re-addition were studied, as likely to be similar to the corresponding reactions of linolic acid. Lewkowitsch<sup>4</sup> states that oleic acid dibromide, on heating with zinc and alcoholic hydrochloric acid, regenerates oleic acid. It was felt, however, that this result required confirmation, in view of the

<sup>1</sup> For tung oil, at least, this not the case.

<sup>2</sup> E. g., Takahashi, *J. Tokyo Chem. Soc.*, 40, 233-89 (1919); *C. A.* 13, 1583 (1919).

<sup>3</sup> A search is at present being made for suitable solid derivatives.

<sup>4</sup> Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Macmillan and Co., London, 1913, Vol. I, p. 184.

known behavior of linolic acid and of the fact that both oleic acid and the two dibromides (oleic and elaidic) are liquids or very low-melting solids, and the identification of the products could accordingly scarcely have been very definite.

In order to obtain more definitely characterizable products, the solid anilides of oleic and elaidic acids were used. The dibromides were obtained both by adding bromine to the anilides in chloroform solution, and by brominating the free acids and subsequently preparing the anilides from the brominated products. The compounds obtained by the two methods were identical.

When oleic acid was converted into the dibromide, treated in the usual way with zinc and alcoholic hydrochloric acid to regenerate the double bond, and then again brominated and converted into the anilide, the only product that could be isolated was oleic-anilide dibromide. As the corresponding elaidic-anilide dibromide is much less soluble, and has a higher melting point, it should have been very easy to recognize, even in rather small amounts, if formed. It is accordingly evident that no elaidic acid was formed.

Similarly, when elaidic-anilide dibromide was boiled with zinc and alcoholic hydrochloric acid, only elaidic anilide was obtained.

It is therefore apparent that when the double bond is regenerated in the dibromides of oleic or elaidic acid (or their derivatives) the original acid is re-formed, without appreciable quantities of the isomeric acid. The cause of this difference between oleic and linolic acid derivatives is still unexplained.

### Experimental Part.

**Oleic-anilide Dibromide.**—Fourteen g. of olive oil fatty acids was dissolved in 30 g. low boiling ligroin, and treated with 1 mol. of bromine in the same solvent, cooling in tap water. The solution was heated on the water-bath for some time with 1 mol. of phosphorus pentachloride, and the phosphorus oxychloride and ligroin were distilled under reduced pressure. The residue was added to 2.5 mols. of aniline, and after standing for some time, the excess of aniline and aniline hydrochloride were removed by washing with dil. hydrochloric acid and with water. The product was crystallized from alcohol after treatment with charcoal. After 6 crystallizations, it melted at 60–62°. Purification from ligroin was considerably more effective, the product melting finally at 67°, after softening at 63°. A sharp melting point could not be obtained.

*Analysis* (Carius). Calc. for dibromo-oleic-anilide: Br, 30.9. Found: 30.0.

The same substance was rather more readily obtained by treating oleic-anilide in 4 parts of chloroform, with 1 mol. of bromine, evaporating the chloroform, and recrystallizing from ligroin. It softened at 64° and melted at 67°, and a mixture of the two products behaved in exactly the same way. It is very soluble in hot alcohol, moderately soluble in the cold, and readily soluble in warm ligroin.

**Bromination of Oleic-anilide in Other Solvents.**—Oleic-anilide in 7 parts of ligroin was treated with 1 mol. of bromine, also dissolved in ligroin. The anilide was not entirely soluble, and apparently an excess of bromine reacted with the soluble portion.

A small amount of a product melting after recrystallization from alcohol at 90–91° was obtained. It was only slightly soluble in cold alcohol, and separated from it as an almost gelatinous mass without apparent crystalline structure. It was, however, readily reduced to a dry powder. The quantity obtained was not sufficient for analysis.

When oleic anilide was treated at room temperature, in chloroform solution, with 4 mols. of bromine (calc. for oleic-tribromo-anilide dibromide), and the solution washed with sodium hydrogen sulfite solution to remove a slight excess of bromine, a different product was obtained, readily soluble in hot alcohol, moderately soluble cold, and melting at 77–78°.

*Analysis* (Carius). Calc. for dibromo-oleic-anilide: Br, 30.9. Calc. for dibromo-oleic-monobromo-anilide: Br, 40.2. Found: 37.15.

The analysis shows the product to be a mixture, and less highly brominated than might have been expected.

**Elaidic-anilide.**—This compound was readily prepared by heating 20 g. of elaidic acid and 15 g. of aniline at 200° for 3 hours in a bomb tube. On recrystallizing from alcohol, the bulky mass of crystals retains an unusually large amount of solvent, so that 3 or 4 crystallizations are necessary. The pure substance melts at 72°, and is readily soluble in hot benzene, moderately soluble cold, very soluble even in cold chloroform, and only slightly soluble in low-boiling ligroin.

**Elaidic-anilide Dibromide.**—This was made in chloroform solution in the same way as the corresponding oleic acid derivative. It is very soluble in chloroform, readily soluble in hot alcohol, slightly soluble cold; and very soluble in hot benzol. The pure substance melted at 88°.

*Analysis* (Carius). Calc.: Br, 30.90. Found: 31.45.

The same substance was obtained as follows. Elaidic acid was converted into the chloride by warming with 1 mol. of phosphorus pentachloride, and the phosphorus oxychloride distilled under reduced pressure. The chloride was taken up in chloroform, 1 mol. of bromine added (with moderate cooling), and after a few minutes, an excess of aniline. The product, after recrystallization from alcohol, was identical with that described above.

**Oleic Acid Regenerated from Oleic Dibromide.**—Twenty g. of oleic acid was brominated in chloroform in the usual manner. The chloroform was distilled and the residue heated for 8 hours under a reflux condenser with an excess of zinc and alcoholic hydrochloric acid. The unsaturated acid thus formed was separated, dried, and converted into the chloride with phosphorus pentachloride, the oxychloride formed being removed under reduced pressure. The chloride was taken up in chloroform and re-brominated, then treated with an excess of aniline. No elaidic-anilide dibromide could be isolated (although it is less soluble and higher melting than the product obtained) the only product isolated being oleic-anilide dibromide, melting, after 3 recrystallizations from ligroin, at 65°.

**Elaidic-anilide from Elaidic-anilide Dibromide.**—Four g. of the dibromide was refluxed for 8 hours with zinc and alcoholic hydrochloric acid. The resulting product was separated and heated for 2 hours with alcoholic potash with the intention of completing the hydrolysis of the anilide. Even after this treatment, however, most of the anilide had resisted hydrolysis. Recrystallized from alcohol and then from ligroin, the elaidic-anilide melted at 67° and was shown by mixing with pure elaidic-anilide to be identical with that substance.

### Summary.

1. The anilides of oleic and elaidic acids and their dibromides have been used to demonstrate definitely that there is no *cis-trans* isomerization

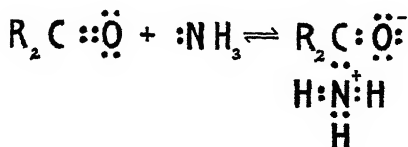
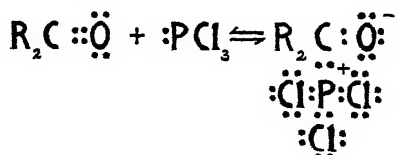
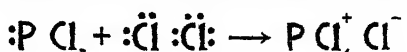
when bromide is added to the double bond and later removed, in the case of either of these acids.

2. This behavior is contrasted with that of linolic acid under similar circumstances.

CHICAGO, ILLINOIS.

### NOTE.

**Correction.**—"Addition Reactions of the Carbonyl Group Involving the Increase in Valence of a Single Atom."<sup>1</sup> Certain typographical errors in three of the formulas given in this article were overlooked. The second



equation on p. 1707, and the first two equations on p. 1708 should read as given above.

JAMES B. CONANT.

### NEW BOOKS.

**John Harper Long.** A Tribute from his Colleagues. Edited by DR. ROBERT H. GAULT, Northwestern University. Northwestern University Press, Chicago, 1921. 70 pp. 15.5 × 22.5 cm. Price \$1.00.

The many friends of the late Professor John Harper Long, for 37 years professor of Chemistry in Northwestern University, will appreciate this feeling portrayal of the man as teacher, investigator, public servant and friend.

This little volume edited by Dr. Robert H. Gault of Northwestern University, contains a chapter by F. B. Dains, entitled "Student, Teacher and Chemist," one by F. Robert Zeit, "A Colleague at the Medical School," another by Ira Remsen on "Dr. Long as a Member of the Referee Board," and an appreciation of the last ten years of Dr. Long's scientific work by Drs. Julius Stieglitz and Paul Nicholas Leach. Dr. Frank Wright reviews

<sup>1</sup> THIS JOURNAL, 43, 1705 (1921).

Dr. Long's activities in connection with Chicago's gigantic drainage problems and the volume concludes with a comprehensive bibliography of Dr. Long's publications, comprising 118 contributions.

There is thus compassed in 70 pages, tastefully arranged, a fitting tribute to a man who did so much for chemistry and education. One outstanding feature of Dr. Long's professional life comes back vividly to the reviewer, a characteristic which indexed well his deep, unselfish interest in his profession, namely, his constant attendance and active, helpful participation in the national and sectional meetings of the American Chemical Society. Even long after his health should have demanded more consideration of self, he gave unstintingly of his time, his counsel and his uplifting ideals, to the organization which had given him his highest honor.

The edition is limited to one thousand, and copies may be obtained through Professor Robert H. Gault, Northwestern University, Evanston, Ill.

W. LEE LEWIS.

**Grundriss der Kolloidchemie.** 6th edition (unchanged reprint of the 5th edition).

By DR. WOLFGANG OSTWALD, Privatdozent at the University of Leipzig. Theodor Steinkopff, Residenzstrasse 12b, Dresden-Blasewitz, Germany, 1921. First half: vi + 329 pp. 60 fig. 16.5 × 24 cm. Price \$2.00.

Colloidal chemistry has developed rapidly during the dozen years that have elapsed since the appearance of the first edition of the "Outline." This development is reflected in the marked expansion shown in this edition, where some 329 pages are required to cover the ground of 140 pages of the first edition.

The mode of treatment, however, is substantially the same as that previously adopted; the subject matter is systematically subdivided in the best Teutonic manner, and each subdivision is thoroughly and carefully discussed in the clear and fluent diction characteristic of the author. The first few chapters of the old edition, dealing with the development of colloid chemistry, have been wholly omitted. It is not too hazardous to predict that, true to hereditary instincts, the author will utilize this product of reproduction by segmentation in an independent volume on the history of colloid chemistry.

The main subdivisions of this first half are: A Practical Introduction; The General Topography of Colloidal Systems; The Relation between the State of Aggregation and the General Properties of Colloidal Systems; The General Energetics of Dispersoids; The Prevalence of the Colloidal Condition, and The Meaning of Colloidal Chemistry; last, The Mechanical Properties of Colloidal Substances.

The paper and type used in this volume leave much to be desired.

ARTHUR B. LAMB.

**Festschrift der Kaiser Wilhelm Gesellschaft zur Förderung der Wissenschaften zu ihrem Zehnjährigen Jubiläum dargebracht von ihren Instituten** (Memorial Volume published by the Kaiser Wilhelm Gesellschaft). Julius Springer, Berlin, 1921. iv + 282 pp. 19 fig. 26 × 18 cm. Price M. 100; bound, M. 130.

This volume celebrating the tenth anniversary of the establishment of the Kaiser Wilhelm Gesellschaft has been issued by its several Institutes. It contains 33 short articles on the most varied topics of Natural Science. These articles have been prepared by leading German investigators. Those of most interest to chemists are:

- Abderhalden.** A Contribution to our Knowledge of Organic Foodstuffs Exhibiting Specific Activity.
- Beckmann.** The Conversion of Grain Straw and Lupine to Foodstuff of Higher Value.
- Einstein.** A Simple Application of Newton's Law of Gravitation to Globular Star Clusters.
- Fischer and Schrader.** A New Hypothesis Regarding the Origin and Structure of Coal.
- Freundlich and Loening.** Protective and Coagulating Action of Hydrophilic Colloids on Hydrophobic Sols.
- Haber.** Science and Economics.
- Hahn.** Regarding Radioactive Disintegration Series and a New Active Substance in Uranium.
- Hofmann and Myron.** The Chemistry of Sodium Phenolate Fusions.
- Polanyi.** The Adsorption of Gases by Solid Bodies.
- Warburg.** The Physical Chemistry of Cellular Respiration.
- v. Wassermann.** Biological Equilibria in Infections and their Medicinal Significance.

The volume is printed elegantly on excellent paper.

ARTHUR B. LAMB.

**Analytische Chemie.** By DR. TH. DÖRING, o. Professor an der Bergakademie Freiberg I. Sa. Theodor Steinkopff, Dresden and Leipzig, Germany. 1921. iii + 97 pp. 15 × 21.5 cm. Price \$0.60.

This book is the first volume of a series of "Wissenschaftliche Forschungsberichte" whose object is to indicate the more important contributions to particular fields of science since 1914. The publication of this series is of interest as indicating the steps which are being taken in Germany to "rehabilitate" research by familiarizing the investigator with recently published data, which may not be readily available to him. The present volume treats developments in analytical chemistry from this standpoint. In the introduction it is suggested that advances in analytical chemistry from the beginning of this century to the outbreak of the World War have been especially noteworthy in three directions: (1) the utilization of special organic reagents, such as cupferron and dimethylglyoxime; (2) improvements in physical instruments and increase in their use; for example, the refractometer, colorimeter, and nephelometer; (3) the in-

creased use of physico-chemical principles, especially in the treatment of volumetric analysis.

The subjects treated are the detection, estimation, and separation of the common elements and a few of the rare ones, together with many inorganic anions. The determination of gases in metals, and the elementary analysis of organic substances are also included.

As in any similar case, the selection of the "more important" contributions is a matter of opinion both in regard to omissions and inclusions, and the judgment of the author will not always coincide with that of the reader. Nevertheless, the fact that there are more than 500 footnote references (including duplicates) and that these contain a liberal admixture of other than German references (about 60% are to German periodicals) indicates that the author has attempted a thorough treatment of his subject.

In a book of 86 pages the discussion of each item is necessarily too brief to include many details of operation. The book should, however, fulfil a useful function for the investigator by giving him suggestions from and references to recent advances in analytical chemistry which he could hardly obtain otherwise except by considerable study of the literature.

GRAHAM EDGAR.

**A French-English Dictionary for Chemists.** By AUSTIN M. PATTERSON, PH. D. John Wiley and Sons, Inc., New York; Chapman and Hall, Limited, London, 1921. xvii + 384 pp. 18 × 12.5 cm. Price \$3.00.

It is a pleasure to welcome a companion volume to Dr. Patterson's useful German dictionary, and the present work embodies the successful features of the other. The book is handy to use, the pages are easy to read at a glance, and the restriction of the vocabulary saves much time and space. In general the selection of words and idioms is excellent, and the translations are accurate.

As Dr. Patterson in his preface invites suggestions, the following points are mentioned.

A current French industrial journal yielded the following words not given in the dictionary: *amodier*, *amodiation*, *acier à coupe rapide*, *déprimomètre*, *remous*. *Calvine* should certainly find a place among medical terms. *Rationnel* means something like "scientific" at least as often as "rational." *Admettre* is insufficiently accounted for by "admit, accept (as true), receive, allow, concede." It often means "postulate," or "suppose." Cf. "Ce chimiste (Avogadro) admit que des volumes égaux . . . contiennent des nombres égaux de molécules." Even though "strong, thick, hard, difficult, severe, skillful, clever" are given for *fort* (a), some such additional adjective as "large" or "great" seems to be necessary in "*une forte proportion*." *Faible* is somewhat better, as we find "slight" as well as "weak" and "feeble," but how about "*la densité du gaz sera plus faible?*" The meaning



"early" for *précoce*, need not have been restricted to "fruit;" it is often applied, for instance, to frost and baldness.

The book is a good one, and will probably be further improved. Chemists who read French need it.

NORRIS F. HALL.

**Die Biogenen Amine und ihre Bedeutung für die Physiologie und Pathologie des Pflanzlichen und Tierischen Stoffwechsels.** (The Biogenic Amines and their Significance for the Physiology and Pathology of Plant and Animal Metabolism.) By M. GUGGENHEIM. Julius Springer, Berlin, 1920. viii + 376 pp. 14.5 X 21.5 cm.

A compilation of the literature on biogenic amines down to the early months of 1919 both from the viewpoint of the chemist and the pharmacologist. The amines are classified as follows: alkyl amines, alkamines, neurine group, diamines, guanidine compounds, amidazol compounds, betaines and  $\alpha$ -amino acids, phenyl-alkyl and phenyl-alkanol amines, indol-ethylamine.

Seventy pages of references are included.

The author has worked extensively in this field, which as stated in his preface, had been well covered in 1914 by Barger's "The Simpler Natural Bases," Longmans, Green and Company, London.

H. G. BARBOUR.



THE JOURNAL  
OF THE  
American Chemical Society  
with which has been incorporated the  
American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

GERMANIUM.<sup>1</sup> I. EXTRACTION FROM GERMANIUM-BEARING  
ZINC OXIDE. NON-OCCURRENCE IN SAMARSKITE.

BY L. M. DENNIS AND JACOB PAPISH.

Received June 25, 1921.

Material.

Argyrodite and canfieldite, which at present are the only minerals known to contain germanium as a definite constituent, are too rare to be regarded as sources of supply of the element. Bardet<sup>2</sup> examined various mineral waters spectroscopically and found that germanium was present in many of them. He succeeded in extracting 60 mg. of germanium dioxide from about 100 kilograms of residues, chiefly calcium carbonate, obtained in the manufacture of Vichy salts from the natural waters. This amount of germanium dioxide represented 250,000 liters of original Vichy water and corresponded to 0.00024 mg. of germanium dioxide per

<sup>1</sup> This article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by Jacob Papish in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Some details of manipulation and additional comments on the history of germanium have been omitted from this article. They will appear in an unabridged version to be published later in the *Zeitschrift für anorganische und allgemeine Chemie*.

<sup>2</sup> Bardet, *Compt. rend.*, **158**, 1278 (1914).

liter of water, a quantity too small to render these waters a practical source of supply of germanium. The extraction of germanium directly from blends, as has been carried out by Urbain, is a very expensive and tedious operation. The most promising source of the element at the present time is the concentrate from certain residues obtained in the smelting of American zinc ores. Buchanan<sup>3</sup> reported that one such residue contained as much as 0.25 % of germanium dioxide. A large supply of this most valuable material was presented to the Department of Chemistry of Cornell University by the New Jersey Zinc Company and the present investigation, as well as others that will follow from this laboratory, would not have been possible except for the generous coöperation of this company. Concerning the origin of this material, Mr. W. M. Kelsey,<sup>4</sup> Superintendent of the Palmerton plant of the New Jersey Zinc Company, states that it was obtained "by a fire concentration of certain residues produced in the ordinary process of smelting for zinc. The original ore was a mixture of high grade sulfides from the Wisconsin and Missouri fields, roughly in the ratio of two parts of Wisconsin ore to one part of Missouri ore."

### Extraction of Germanium.

None of the various methods that were employed by Winkler for the extraction of germanium from argyrodite is adapted to the separation of the element from the germanium-bearing zinc oxide, because the association of elements in this latter material is quite different from that in argyrodite. Zinc oxide is, of course, present in preponderating amount and the concentrate further contains considerable quantities of lead, arsenic, and cadmium, and also traces of other elements, among them being indium, tin, and antimony.

Preliminary trials were made of a variety of possible methods of separation, but as none of these was found to be satisfactory, descriptions of them will not be given here. The procedure that was finally adopted is based upon the volatility of germanium tetrachloride, and is an elaboration of the method described by Buchanan.<sup>3</sup> The essential features of this process consist in treating the crude zinc oxide with hydrochloric acid and then distilling the germanium tetrachloride in a current of chlorine. The chlorine maintains the arsenic in pentavalent form and thus prevents the distillation of arsenic trichloride with the germanium tetrachloride.

In the first trials of this method, portions of the crude zinc oxide of from 250 to 1000 g. each were treated with hydrochloric acid, chlorine gas was passed through the apparatus, and the mixture was heated to effect the distillation of the germanium tetrachloride. This gave a product substantially free from arsenic, but the necessity for long passage of large

<sup>3</sup> Buchanan, *J. Ind. Eng. Chem.*, 8, 585 (1916); 9, 661 (1917).

<sup>4</sup> Letter to L. M. Dennis, September 3, 1919.

amounts of chlorine through the apparatus rendered the procedure unsuited to the extraction of germanium on a large scale from several hundred pounds of the crude material. Browning and Scott<sup>5</sup> substituted potassium permanganate, manganese dioxide, potassium chlorate, or potassium dichromate for chlorine. They used the method for the detection of germanium in very small samples that contained less than a gram of arsenic trioxide or pentoxide and not more than 5 mg. of germanium. But even so they found that when from 0.3 to 0.5 g. of  $\text{As}_2\text{O}_3$  was used, some arsenic appeared in the distillate. It is apparently essential that if the formation of arsenic trichloride and its consequent appearance in the distillate are to be avoided, the concentration of chlorine must be high throughout the whole distillation.

Fresenius<sup>6</sup> states that when a mixture of sodium arsenate and conc. hydrochloric acid is distilled, small amounts of arsenic are volatilized. Mayrhofer<sup>7</sup> in attempting to remove arsenical impurities from hydrochloric acid noticed that even when the acid was first treated with chlorine or when some pyrolusite was added to the acid and it was then distilled, small amounts of arsenic were always found in the distillate. Hehner<sup>8</sup> distilled arsenic acid with strong hydrochloric acid and obtained comparatively large quantities of arsenic in the several fractions of the distillate. He states that "a similar result was obtained when potassium permanganate had been added before the beginning of the distillation, or, in other words, when the distillation was begun in the presence of chlorine."

In an investigation of the reaction between hydrogen sulfide and arsenic pentoxide in the presence of hydrochloric acid, Usher and Travers<sup>9</sup> studied the reaction between arsenic pentoxide and hydrogen chloride in sealed tubes. They concluded that the reaction is that expressed by the equation  $\text{As}_2\text{O}_5 + 10\text{HCl} \rightleftharpoons 2\text{AsCl}_3 + 2\text{Cl}_2 + 5\text{H}_2\text{O}$ , the equilibrium shifting rapidly to the right with increasing concentration of hydrogen chloride.

These observations upon the reduction of arsenic pentoxide by conc. hydrochloric acid and volatilization of arsenic trichloride when such a mixture is distilled, have been sustained by the experimental evidence accumulated in this laboratory during the progress of the investigation here described. When potassium permanganate was added to the crude zinc oxide and this was then distilled with an excess of conc. hydrochloric acid, arsenic trichloride passed into the distillate. To maintain the concentration of chlorine, the procedure was modified by slowly running into the flask a solution of the potassium permanganate during the distillation with hydrochloric acid. It was found that the dilution of the acid soon rose to such an amount that the germanium tetrachloride instead of distilling off was hydrolyzed in the flask. To ascertain whether a mixture of sodium arsenate and sodium germanate, when distilled with an excess of conc. hydrochloric acid, would yield arsenic trichloride in the distillate, a mixture of the oxides of arsenic and germanium was fused with a slight excess of sodium peroxide, the fused mass was dissolved in water and the solution was heated to boiling. It was then cooled, and excess of hydrochloric acid was added and the liquid was distilled. The distillation gave a yellow precipitate with hydrogen sulfide which indi-

<sup>5</sup> Browning and Scott, *Am. J. Sci.*, [4] 44, 313 (1917); 46, 663 (1918).

<sup>6</sup> Fresenius, *Z. anal. Chem.*, 1, 447 (1862).

<sup>7</sup> Mayrhofer, *Ann.*, 158, 326 (1872).

<sup>8</sup> Hehner, *Analyst*, 27, 268 (1902).

<sup>9</sup> Usher and Travers, *J. Chem. Soc.*, 87, 1370 (1905).

cated the presence of arsenic. In another experiment lead dioxide was used in place of sodium peroxide. Arsenic here also passed into the distillate. These experiments, as well as the observations of previous investigators, indicate that arsenic acid is reduced to arsenic trichloride during distillation with hydrochloric acid unless a high concentration of chlorine throughout the distillation is maintained.

To ascertain whether arsenic trioxide when dissolved in sodium hydroxide, saturated with chlorine, and then acidified with hydrochloric acid, would yield any arsenic trichloride when distilled in a current of chlorine, 5 g. of arsenic trioxide was dissolved in 20 cc. of a 30% solution of potassium hydroxide, this solution was saturated with chlorine, and then, without interrupting the current of chlorine, 190 cc. of pure conc. hydrochloric acid was added and the liquid was distilled. A Reitmaier-Stutzer bulb was used to prevent so far as possible the mechanical passage of some of the liquid into the distillate. Two fractions of 40 cc. each were obtained. Each of these was saturated with hydrogen sulfide. After 12 hours there separated a few small yellow particles that resembled sulfur. These were tested for arsenic by heating them with nitric acid, adding ferrous sulfate to reduce the nitric acid, then adding dil. sulfuric acid and warming the mixture to remove oxides of nitrogen, and finally subjecting the material to the "modified Gutzzeit test."<sup>10</sup> The reaction was allowed to proceed for 10 minutes but no discoloration of the crystal of silver nitrate was discernible.

Müller,<sup>11</sup> in a recent article upon the atomic weight of germanium, states "The chlorine—hydrochloric acid distillation process, though adequate for the removal of silica and tin, can hardly be accepted as a means of eliminating the last traces of arsenic from germanium compounds. Four redistillations of the chloride from hydrochloric acid solution in a stream of chlorine failed to remove the last of the arsenic." Careful perusal of his article fails to reveal experimental support for this statement. In fact, in his description of the purification of germanium, he remarks that the precipitation of redistilled germanium tetrachloride by hydrogen sulfide yielded a "snow-white germanium sulfide." The point is of importance, and the possible presence of arsenic in the distilled germanium tetrachloride will be followed carefully during further work in this laboratory.

To avoid the necessity for the use of the very large amounts of chlorine that would be called for if the germaniferous zinc oxide were directly distilled with hydrochloric acid in a current of chlorine for the separation of germanium, it was decided to distil germanium tetrachloride and arsenic trichloride together from the crude zinc oxide and thus to effect, as a first step, the separation of the germanium from the large amount of the zinc oxide that is present in the original material.

### Apparatus.

The unit still consists of a round-bottom 5-liter Pyrex flask supported on an asbestos "collar"<sup>12</sup> 10 cm. high, the collar resting on an iron plate and this on a strong tripod. A 2-hole rubber stopper in the neck of the

<sup>10</sup> Dennis and Whittelsey, "Qualitative Analysis," Ginn and Co., Revised Ed., p. 31.

<sup>11</sup> Müller, *THIS JOURNAL*, 43, 1085 (1921).

<sup>12</sup> This device for heating glass or porcelain vessels that contain a mixture of liquid and solid materials has been in use in the Cornell Laboratory for several years. A

flask carries a bent glass tube for connection with a Liebig condenser, and through the other opening of the stopper is inserted a short glass tube through which the desired amount of conc. hydrochloric acid may be blown into the flask by air pressure from a large graduated bottle. After the acid has been driven into the flask in the actual operation, the glass tube is replaced by a solid glass plug. A bent glass tube is attached to the farther end of the condenser by means of a short piece of rubber tubing. This glass tube is about 10 mm. in diameter and reaches nearly to the bottom of a 4-liter bottle which serves as a receiver. The iron plate upon which the collar rests is heated with a large Meker burner, and to avoid loss of heat, the tripod is surrounded by sheets of asbestos board. The duration of each distillation is further shortened by covering the upper part of the flask with an asbestos jacket. This jacket is made by first covering that part of the flask which projects above the collar with a layer of moist filter paper. Asbestos felt which had been soaked in water is then laid upon the paper in over-lapping pieces and smoothed down to an even, continuous layer. Wet asbestos cement is then laid over the whole exterior of the jacket. The opening in the top of the jacket is made sufficiently large to permit of the removal of the cap from the flask. The cap is allowed to dry on the flask and is then removed and its lower edge and the upper rim are dipped in a solution of sodium silicate to stiffen them. The receiver stands in an earthenware jar.

### Distillation.

One kilogram of the crude zinc oxide is introduced into the flask, water is placed in the receiver to such a depth as just to cover the end of the glass tube, and the earthenware jar in which the bottle stands is filled with cracked ice. Twenty-five hundred cc. of commercial conc. hydrochloric acid (1.18 sp. gr.) is next driven into the flask through the glass tube in the stopper, and the tube is then replaced by a solid glass plug. The heating of the flask is begun and continued until 2000 cc. of the distillate has collected, this amount having been shown spectroscopically to suffice for the recovery of all the germanium.

"collar" is made from asbestos board 3 to 6 mm. thick, a strip of the board of the desired width being first thoroughly wet with water, then bent into a circle and fastened at the over-lapping ends with iron or copper wire, and finally dried. The "collars" may of course be made of any desired diameter. The collar is placed upon an iron plate about 3 mm. thick and this plate rests in turn upon an iron tripod. If the collar is dipped in a dilute solution of sodium silicate, it becomes stiff when dry, and although somewhat brittle, its life is prolonged by this treatment. A glass flask or porcelain evaporator placed on one of these collars does not come into direct contact with the gas flames under the iron plate, and local heating that would result from the direct application of the flame to the container, which often causes the fracture of the vessel, is thus avoided. The collar is especially useful in the long digestion of a powdered mineral with acids.

### The Precipitation of Germanium and Arsenic by Hydrogen Sulfide.

The acid distillate may now be treated with hydrogen sulfide in such manner as to precipitate all of the arsenic and germanium that are present, or the conditions may be so regulated as to cause the precipitation of arsenic trisulfide alone or mixed with only a very small amount of germanium sulfide. This last procedure was used by Winkler<sup>13</sup> and is now being studied in this laboratory. The method that we have employed up to the present time involves the simultaneous precipitation of the sulfides of germanium and arsenic.

Successive distillates are poured into a 15-liter glass bottle until about 10 liters of the solution has been collected. Since the precipitation of germanium disulfide is most complete when the acid concentration is about 6 *N*, conc. sulfuric acid is slowly added to the contents of the bottle until the acidity is brought to about this point. The acid is run in from a separatory funnel that passes through one opening of a 2-hole rubber stopper inserted in the neck of the bottle. Loss of germanium tetrachloride that might be volatilized during the addition of the sulfuric acid is avoided by placing in the other opening of the stopper a short, bent delivery tube that dips into a liter of 6 *N* sulfuric acid that has been saturated with hydrogen sulfide. Washed hydrogen sulfide is now passed through this solution. Yellow sulfide of arsenic is first precipitated. White germanium disulfide next appears, and if the liquid is not agitated, this white sulfide separates as a distinct layer on the top of the yellow sulfide of arsenic. When precipitation is complete, the large bottle is stoppered and is allowed to stand for 24 hours. The contents of the bottle is then brought upon a filter and the sulfides are washed with the aid of suction with 3 *N* sulfuric acid that has been saturated with hydrogen sulfide.

The filtrate from the sulfides of germanium and arsenic is placed in a large bottle or in a tall, covered, glass cylinder and allowed to stand for 48 hours. At the end of this time a slight precipitate of the sulfides separates. The supernatant liquid is then siphoned off and the bottle or cylinder is filled with the filtrate from the next precipitation which is again allowed to stand for 48 hours. When a fairly large amount of the sulfides has accumulated in the vessel, it is brought upon a filter and washed as before. The amount of germanium that is recovered by this treatment averages about 2 mg. for every liter of filtrate.

From this point forward two different procedures have been followed. In the first of these the moist sulfides are dissolved in a 50% solution of sodium hydroxide with the aid of heat. Successive portions of the sulfides are added to this solution until a small amount is left undissolved.

<sup>13</sup> Winkler, *J. prakt. Chem.*, **142**, 194 (1886).



This is then taken into solution by the addition of a little more of the concentrated solution of sodium hydroxide and then about 8 g. of solid sodium hydroxide is added to render the solution strongly alkaline which facilitates the later oxidation of the arsenic. This solution is then placed in a Pyrex flask which is provided with a rubber stopper that carries a delivery tube, a separatory funnel, and a glass tube that reaches nearly to the bottom of the flask. This last tube has a wider tube fused to its lower end to avoid stoppage. The flask is placed on an asbestos collar and is connected with a condenser and a receiver in the manner above described. Washed chlorine is then passed through the liquid in the flask to convert the arsenic to the pentavalent form. When the contents of the flask has been saturated with chlorine and the apparatus is filled with the gas, the speed of the flow of chlorine is lessened and conc. hydrochloric acid is run into the flask through the separatory funnel until the acid is in large excess. The flask is then heated and the germanium tetrachloride is distilled in a slow current of chlorine, the distillation being continued until half of the liquid in the flask has passed over.

The larger part of the germanium tetrachloride passes over between  $90^{\circ}$  and  $100^{\circ}$ . Instead of collecting the germanium tetrachloride as such from this distillation, some water is placed in the receiver to hydrolyze the compound. The resulting hydrated germanium dioxide is pure white in color. If any of the oily tetrachloride is seen to collect under the layer of liquid on the bottom of the receiver during the distillation, it is an indication that the concentration of hydrochloric acid in the receiver is so high as to repress the hydrolysis of the germanium tetrachloride. In such case more water is poured into the receiver. When half of the liquid in the flask has passed over, the receiver is removed and a fresh receiver containing some water is put in its place. A volume of conc. hydrochloric acid equal to the volume of the liquid that has distilled over is now run into the flask through the separatory funnel and the distillation is continued. When half of the liquid now in the flask has distilled over, most of the germanium tetrachloride has usually passed into the distillate, but it was found that complete separation of that element as the tetrachloride is effected only by many repetitions of the distillation.

The hydrated germanium dioxide is now collected on a small disk of filter paper supported by a Witt plate in a large funnel and is washed first with dil. sulfuric acid and then with small portions of cold water. It is transferred to an evaporating dish and is dried in an air bath at a temperature of  $110^{\circ}$ . Photographs of the arc spectra of various portions of this material showed that the germanium dioxide contained traces of sodium, calcium, and iron. Fractional precipitation of a solution of a sample of the dioxide by hydrogen sulfide failed to disclose the presence of arsenic.

Germanium in the filtrate and washings from the hydrolyzed germanium dioxide is recovered by precipitation with hydrogen sulfide.

To free the germanium dioxide from the traces of impurities noted above, it is dissolved in a slight excess of sodium hydroxide with the aid of heat, the solution is treated with chlorine in the manner above described, hydrochloric acid is added, and the germanium tetrachloride is again distilled in a current of chlorine and is hydrolyzed as before.

The above method for the separation of germanium and arsenic gives quite satisfactory results in respect to the completeness of the recovery of the germanium, but it is open to the following objections.

The precipitate of the mixed sulfides contains a preponderating amount of arsenious sulfide. This necessitates the use of large quantities of sodium hydroxide, chlorine, and hydrochloric acid, and greatly lengthens the time of treatment with chlorine. Again, the addition of hydrochloric acid to the chlorinated solution of the mixed sulfides in sodium hydroxide reprecipitates a part of the sulfides, and the conversion of the germanium in this precipitate into the volatile germanium tetrachloride by the action of hydrochloric acid and chlorine proceeds very slowly. Furthermore, a large amount of arsenic in the precipitate causes the appearance of some of that element in the distillate even though the current of chlorine through the apparatus is not interrupted during the distillation. This fact necessitates a second precipitation of the sulfides of germanium and arsenic and a redistillation in chlorine in order to free the germanium completely from arsenic.

It is evident that these difficulties would largely be obviated if the greater part of the arsenic could be separated from the germanium before distillation in chlorine. Preliminary experiments indicated that this separation could be accomplished by roasting the dried sulfides in air and this led to the development of the second procedure for the treatment of the mixed sulfides which is as follows.

If the mixed sulfides of germanium and arsenic are to be roasted, it is, of course, essential that the sulfide precipitate be washed free from chlorides before the roasting to avoid loss of germanium through volatilization of germanium tetrachloride. To this end the washing of the sulfides with 3 *N* sulfuric acid is continued until the chlorides are completely removed. The absence of chlorides in the wash-water is ascertained by adding cadmium nitrate to a portion of the liquid to precipitate the hydrogen sulfide, filtering off the precipitate, and then adding silver nitrate to the filtrate. The washed sulfides are transferred to a large evaporating dish and are dried in an air-bath at 110°.

The dried sulfides consist of from 78 to 90% of arsenious sulfide, the remainder being germanium disulfide and moisture, together with small quantities of sulfur and sulfuric acid. These dry, crude sulfides are placed in shallow iron dishes and are roasted in a muffle furnace at a tempera-

ture not to exceed 500°. This removes the greater part of the arsenic.

Up to 500° there is no loss of germanium, as shown by examining spectrographically the sublimate on a sheet of aluminum placed above the iron dish. At slightly above 600° there is a 30% and at 800–900° about a 90% loss of the germanium.

Each of three 100g. samples of the dried, crude sulfides yielded, on roasting, about 24 g. of the germaniferous residue. The actual decrease in the amount of arsenic was, however, greater than this difference of weight indicates, because of the formation of a considerable amount of iron oxide during the roasting. The extent of the removal of arsenic was approximately ascertained by determining the amount of arsenic in an unroasted sample and in that sample after roasting. Before roasting, the material contained 78.2%, and after roasting, 5.52% of arsenic calculated as the trisulfide,  $As_2S_3$ . These results indicate that somewhat over 90% of the arsenic is removed by this treatment.

The germanium in this residue is extracted by dissolving the finely pulverized material in a 50% solution of sodium hydroxide, chlorinating the solution, adding two parts by weight of conc. hydrochloric acid to every one part by weight of the roasted residue, and distilling. Usually, this completely removes the germanium and no more than faint traces of arsenic are found in the distillate. The resulting hydrated germanium dioxide is freed from the last traces of arsenic by dissolving it in sodium hydroxide, chlorinating the solution, and again distilling with hydrochloric acid in a current of chlorine.

This procedure of first roasting the mixed sulfides to remove the greater part of the arsenic and then distilling the germanium tetrachloride from the residue is superior to the first method of directly distilling the germanium tetrachloride from the mixed sulfides in that the consumption of materials is less, the time needed for the distillation is much shorter, and the separation from arsenic is more complete. It possesses, however, one drawback, the necessity of washing the mixed sulfides free from chlorides before roasting. If a small sample of the sulfides be washed with 3 N sulfuric acid that has been saturated with hydrogen sulfide, chlorides can be removed quite completely and the filtrate is free from detectable amounts of germanium, but it was found that when this method was used on a large scale, repeated washing with 3 N sulfuric acid yields eventually a milky filtrate which slowly deposits white germanium sulfide when its acidity is brought up to 6 N. 5 N sulfuric acid saturated with hydrogen sulfide was substituted for the 3 N acid. This gave a clear filtrate from which no appreciable amount of germanium sulfide separated on standing, but the removal of the chlorides was very slow. Attempts to wash the precipitated sulfides with 5 N sulfuric acid by decantation led to no satisfactory results.

Either of the above processes yields a very pure germanium dioxide. The first gives a somewhat higher yield and the second procedure is considerably shorter. The precipitation of arsenic trisulfide substantially free from germanium sulfide from weakly acid solutions is now being studied in the hope that a procedure superior to either of those above described may be developed.

### The Determination of Germanium.

To gage the efficiency of the extraction of the germanium from the crude material, it was necessary to develop a method for the quantitative determination of germanium. The procedure that was finally adopted is based directly upon the method of extraction that has already been described.

A weighed quantity, 20 to 100 g., of the germaniferous zinc oxide that had been dried at  $110^{\circ}$  is ground into a paste with water and is then poured into a flask that contains a solution of sodium hydroxide. These three substances are used in the proportions of 1 part of sodium hydroxide, 2 parts of the crude zinc oxide, and 5 parts of water. The flask is provided with a 3-hole rubber stopper through which are inserted a glass tube that reaches almost to the bottom of the flask, a small Vigreux distilling column, and a small separatory funnel. To the side arm of the Vigreux tube is fused a Liebig condenser, and a glass adapter is fused to the further end of the condenser. The receiver consists of an Erlenmeyer flask that is provided with a 2-hole rubber stopper. Through one of these holes passes the glass adapter which reaches to within a few millimeters of the bottom of the flask. A delivery tube is inserted through the other hole of the stopper and this tube is connected with a second Erlenmeyer flask. Water is placed in the first Erlenmeyer flask to a depth of 3 cm. and the second flask is half filled with water. The second flask serves as a check upon the completeness of the stoppage of germanium chloride in the first receiver. If any germanium is later found to have passed into the second flask, the determination is rejected. Both flasks are placed in a trough containing ice water.

In beginning the distillation a dish containing cracked ice is brought up under the distilling flask, and the apparatus is filled with chlorine which indicates that the contents of the flask has been saturated with the gas. Pure, conc. hydrochloric acid is next slowly introduced through the separatory funnel in amount sufficient to neutralize the sodium hydroxide that was originally employed and, in addition, to equal twice the weight of the crude zinc oxide that is being used. The passage of chlorine and the cooling of the flask are continued during the addition of the acid. When all of the acid has been introduced, the dish of cracked ice is replaced by an asbestos collar and the contents of the flask is then heated

in the manner already described. When  $\frac{1}{2}$  of the liquid has distilled over, an equal volume of conc. hydrochloric acid is run into the flask and the distillation is continued until  $\frac{1}{2}$  of the liquid has again passed over. The addition of hydrochloric acid and distillation of  $\frac{1}{2}$  of the liquid are once more repeated. The heating is then stopped and the two receivers are disconnected. Sulfuric acid is added to the contents of each to bring the acidity to 6 *N*, the flasks standing in ice during the addition of the acid. The liquid in each flask is then saturated with hydrogen sulfide and the flasks are stoppered and set aside for 24 hours. If the passage of the chlorine through the apparatus during the distillation has been slow, and if the receivers have been kept well cooled with ice, no germanium tetrachloride will pass over into the second receiver. A precipitate will, however, appear in the second flask because of the liberation of sulfur through the interaction of chlorine and hydrogen sulfide. The precipitate is tested spectrographically to ascertain whether it is free from germanium. If it is not, the determination is rejected. The precipitated germanium disulfide in the first flask is brought upon an ashless filter paper and the small amount of precipitate that adheres to the walls of the flask is loosened by means of a rubber "policeman" and brought upon the filter by rinsing with 3 *N* sulfuric acid that has been saturated with hydrogen sulfide. The whole precipitate is now washed with this liquid until the chlorides are removed. The germanium disulfide is then washed with alcohol to remove the sulfuric acid and is next dried. The bulk of the precipitate is removed from the filter and placed in a weighed porcelain crucible. It is moistened with nitric acid (1:1), the crucible is gently heated until the liquid has been driven off, is then allowed to cool, and conc. nitric acid is added. This is also driven off by gentle heating and the crucible is finally heated to dull redness.

Germanium dioxide that has been dried at 110° still contains an appreciable amount of water. Experiments performed in this laboratory by Miss K. M. Tressler, which will be described in a later article, have shown that complete dehydration is secured only when the dioxide is heated to 900°.

The filter paper is incinerated over a second weighed crucible. The product is black, due to the formation of some germanous oxide caused by the reduction of the germanium dioxide by the carbon of the paper. This is oxidized to the dioxide by treatment with nitric acid.

The filtrate from the precipitation of the germanium disulfide is set aside for 48 hours and the precipitate that then appears is treated in the same manner as the first precipitate. The sum of the weight of the dioxide in the two crucibles less the weight of the ash of the two filter papers gives the weight of the germanium calculated as dioxide that is present in the original sample.

Although no great accuracy is claimed for the method as thus far developed, two determinations in duplicate of the germanium in different samples of the crude zinc oxide gave concordant results.

Sample I.	I.	II.
Weight of sample, g. ....	50	75
GeO <sub>2</sub> found, g. ....	0.1235	0.1860
GeO <sub>2</sub> , %.....	0.247	0.248
Sample II.		
Weight of sample, g. ....	50	100
GeO <sub>2</sub> found, g. ....	0.0950	0.1885
GeO <sub>2</sub> , %.....	0.19	0.188

The completeness of the recovery of germanium from the crude zinc oxide by the method of extraction above described is evidenced by the fact that from a series of runs in which a total of about 10.7 kilograms of Sample I of the undried, crude oxide was used, 25.936 g. of pure germanium dioxide was obtained.

### The Non-Occurrence of Germanium in Samarskite.

Khrushchov<sup>14</sup> has stated that he had found germanium in American samarskite. This statement was published in the form of a report in the *Journal of the Russian Physical-Chemical Society*.<sup>15</sup> Literally translated it reads as follows.

"K. D. Khrushchov reports about finding germanium in columbium and tantalum minerals. American samarskite was heated in a 300g. platinum crucible for the purpose of comminuting the samarskite. After three heatings, the platinum was altered to such an extent that the crucible crumbled to a powder. On dissolving the platinum, a residue was obtained which resembled silica, but it was fairly difficultly soluble in hydrofluoric acid. Assuming the gelatinous sediment to be germanium dioxide, the reporter found that it was changed very easily by hydrogen to the black powder of germanium. Traces of germanium were also found in tantalite, fergusonite, columbite, gadolinite and in other minerals. American samarskite contains up to 1.5% of germanium. In view of the rarity of argyrodite the reporter calls attention to samarskite as an important source of germanium."

Lincio<sup>16</sup> failed to find evidence of the presence of germanium in samarskite. After the method for determining germanium that has been described in the preceding pages had been developed, the question of the occurrence of the element in American samarskite was taken up in this laboratory. Two hundred g. of finely-ground, selected samarskite was

<sup>14</sup> Khrushchov, *J. Russ. Phys. Chem. Soc.*, [1] 24, 30 (1892).

<sup>15</sup> We are indebted to the Library of Congress for a pen copy of this report. The translation here given was made by one of us (J. P.).

<sup>16</sup> Lincio, *Zentr. Min.*, 1904, 142.

fused with 1200 g. of potassium hydrogen sulfate. The fused mass was extracted with water and the residue, which contained a small quantity of undecomposed samarskite, was mixed with more potassium hydrogen sulfate and was fused and extracted with water as before. The two water extracts were combined and were evaporated to dryness.

The insoluble residue from the fusion was moistened with nitric acid and was then introduced into a Pyrex flask of 500cc. capacity. Two hundred cc. of hydrochloric acid was added and the mixture was subjected to distillation until 150 cc. of distillate had passed over. The distillate was saturated with hydrogen sulfide and was allowed to stand for 24 hours. The very slight precipitate that formed was collected on a small filter and was dried. The photograph of the arc spectrum of this material failed to show the presence of germanium.

The residue obtained from the water extracts of the fused material was moistened with nitric acid, and was introduced into a flask of 3 liters capacity. Fifteen hundred cc. of conc. hydrochloric acid was added and the mixture was distilled until about 600 cc. had passed over. Five hundred cc. of hydrochloric acid was then run into the flask and a second distillate of 400 cc. was obtained. The two distillates were united, were saturated with hydrogen sulfide and were allowed to stand for 24 hours. The slight precipitate that separated showed no spectrographic evidence of the presence of germanium.

Khrushchov's report is by no means convincing. He obtained a gelatinous residue which he assumed to be germanium dioxide, but he gives no reasons for this assumption and it is difficult to imagine what his reasons might have been. The fact that the material was darkened when heated in hydrogen might indicate the presence of a variety of compounds other than germanium dioxide. Moreover, it is probable that when he dissolved the platinum, he used aqua regia for this purpose. If he did so, all of the germanium would probably have been lost through volatilization of the germanium tetrachloride. It seems evident, therefore, that Khrushchov's experimental work does not justify his statement that samarskite contains germanium, and the results obtained by Lincio and in this laboratory would seem to show that that mineral does not carry detectable amounts of the element.

### Summary.

This article contains (1) the details of an experimental study of the extraction of germanium from germanium-bearing zinc oxide, and the preparation of pure germanium dioxide; (2) a description of a method for the determination of germanium; (3) the details of an examination of American samarskite which showed that the mineral does not contain germanium in an amount detectable by means of the spectroscope.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## HEAT OF WETTING OF SILICA GEL.

BY W. A. PATRICK AND F. V. GRIMM.

Received June 25, 1921.

The present investigation was undertaken with a view to ascertaining whether or not it was possible to account for the heat of wetting of silica gel on the basis of the changes of surface energy involved. There is available considerable experimental material,<sup>1,2,3</sup> relative to the heats of adsorption and wetting with adsorbents other than silica gel, and the interpretation of the results has been usually that of an effect due to the compression of the adsorbed liquids. The strongest evidence in favor of this view has been the fact that the heat of wetting by water was found to be negative between 0° and 4°.

Inasmuch as our ideas of the mechanism of adsorption have emphasized the attractive forces between the molecules of the adsorbed substance rather than that between the latter and the adsorbent, it was very difficult for us to accept the above explanation of the heat of wetting. We accordingly planned to measure the heats of wetting of silica gel by a number of liquids with a view to ascertaining whether the observed results were in accord with the involved changes in surface energy.

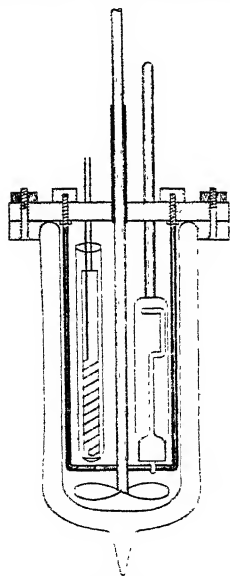


Fig. 1.

It was our belief that by using an adsorbent such as silica gel we could observe an easily measured heat of wetting by a material of definite and known composition. Furthermore inasmuch as the surface presented by such a gel is a water surface, we would be in a position to evaluate the changes in surface energy involved provided the interfacial surface tensions and their temperature coefficients were known.

The calorimeter used in these measurements was a 150cc. Dewar bulb fitted tightly with a hard rubber cover. Although the main portion of the heat of wetting developed within 5 minutes, nearly an hour was required for the calorimeter to give constant readings. For this reason it was thought best to carry out the measurements adiabatically. The calorimeter was accordingly placed in a wooden box which was provided with a fan for stirring the air, and

<sup>1</sup> Jungk, *Pogg. Ann.*, 125, 292 (1865).<sup>2</sup> Schwalbe, *Ann. Physik.*, 16, 32 (1905) (Bibliography).<sup>3</sup> Lamb and Coolidge, *THIS JOURNAL*, 42, 1146 (1920).



electric lamps for heating purposes. It was found that by working with a constant room-temperature of about one degree below that at which the measurement was made it was possible to keep the temperature of the air-bath to within  $0.01^\circ$  or  $0.02^\circ$  of the temperature of the calorimeter. By this arrangement the loss due to radiation was minimized.

The silica gel was placed inside the calorimeter before mixing with the liquid, thus insuring an initial constant temperature. The arrangement by means of which this was accomplished is best seen from the drawing (Fig. 1).

The vessel which contained the gel was provided with a carefully ground glass-stopper. Upon turning and lifting the glass rod sealed to the bottom of the vessel, the gel was thrown into the liquid. A glass hook attached to the stopper enabled the gel to be completely removed from the bottle.

A light stirrer made of glass and turned at a speed of about 500 r. p. m. gave very satisfactory results. A correction of from  $0^\circ$  to  $0.003^\circ$  per minute was applied to take care of the heat due to the stirring alone. The correction varied with the different liquids and was determined separately for each measurement.

The heating unit used for determining the thermal capacity of the calorimeter was constructed similarly to the one used by Tucker<sup>4</sup> in his heat of dilution experiments. It consisted of a Nichrome wire wound around a thin strip of mica and immersed in a thin-walled glass tube filled with oil. Copper leads were brazed on the resistance wire and the former alone extended out of the calorimeter.

A  $5^\circ$  Beckmann thermometer (not shown in Fig. 1) was used to read the temperature of the calorimeter and could be read to within  $0.002^\circ$ . A similar thermometer was placed in the air-bath.

The thermal capacity of the calorimeter was determined with the same charge in the calorimeter after a measurement of the heat of wetting by water had been made. Proceeding in this manner it was unnecessary to know the specific heat of the gel. An electric current from a storage battery was passed through the heating unit for a period of 5 minutes, the exact time being determined with a stop-watch. The resistance of the coil was determined and found to be 1.475 ohms. Current was measured with a milliammeter, readings being taken every 15 seconds. The thermal capacities of liquids other than water were calculated from their specific heats and densities. In all the experiments the same volume of liquid was used, namely, 50.07 cc. Furthermore, conditions were so arranged as to bring the final temperature to  $25^\circ$  in each measurement.

TABLE I.  
EVALUATION OF WATER EQUIVALENT OF CALORIMETER.

Resistance of coil.	Time. Seconds.	Amperes. Average.	Temperature increase.	Cal./degree.
1.475	270.6	1.0717	1.728	63.46
1.475	300.0	1.0920	1.987	63.53
1.475	300.0	1.0701	1.910	63.44

Av. 63.48

<sup>4</sup> W. S. Tucker, *Trans. Roy. Soc.*, 215, 319 (1915).

Taking 0.99681 as the density and 0.99765 as the specific heat of water at 25° the water equivalent of the calorimeter becomes 13.686 cal./degree.

The following values of specific heat and density at 25° were used in the calculation of the thermal capacity of the other liquids.

	Specific heat.	Density.
Ethyl Alcohol.....	0.610	0.785
Benzene.....	0.3921	0.874
Carbon tetrachloride.....	0.2018	1.608
Aniline.....	0.509	1.022

TABLE II.  
HEAT OF WETTING.

Liquid.	Gel used. G.	Temp. rise (corrected). ° C.	Thermal capacity of calorimeter.	Heat of wetting. Cal./g. Gel.	Average.
Water.....	2.4528	0.766	63.48	19.83	
	2.3138	0.700	63.48	19.25	
	2.3795	0.711	63.48	18.97	
	2.4841	0.742	63.48	18.96	
	2.4647	0.745	63.48	19.19	
	2.4602	0.742	63.48	19.15	19.22
C <sub>2</sub> H <sub>5</sub> OH.....	2.4704	1.432	37.75	21.88	
	2.4783	1.512	37.75	23.03	
	2.4605	1.482	37.75	22.74	
	2.4789	1.498	37.75	22.81	
	2.4826	1.495	37.75	22.73	22.63
C <sub>6</sub> H <sub>6</sub> .....	2.4575	0.898	30.85	11.27	
	2.4668	0.872	30.85	10.66	
	2.4746	0.912	30.85	11.37	
	2.4771	0.901	30.85	11.22	11.13
CCl <sub>4</sub> .....	2.4772	0.724	29.93	8.75	
	2.4654	0.686	29.93	8.33	
	2.4804	0.697	29.93	8.41	
	2.4821	0.678	29.93	8.18	8.42
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> .....	2.4890	1.078	39.73	17.21	
	2.4842	1.082	39.73	17.31	
	2.4822	1.134	39.73	18.15	
	2.4938	1.098	39.73	17.50	17.54

The heat of wetting by water was also determined between 0° and 4° and in all cases the results were positive. At 2.86° with 2.48 g. of gel the temperature increased to 3.92° within the first 5 minutes. Due to the fact that we did not try to make the calorimeter adiabatic, no effort was made to secure an exact value of the heat of wetting at this temperature.

With aniline the wetting was much slower and required about 2 hours before the temperature readings were constant.

### Discussion.

The fact that the heat of wetting by water between 0° and 4° was found to be positive is in itself considerable evidence against the compression theory of the heat of wetting.

There remains however the fact that a number of investigators have shown that the heat of wetting is negative between 0° and 4°. On closer examination it is evident that such experimentors were dealing with an effect of an entirely different order of magnitude. For example G. Schwalbe<sup>2</sup> in order to detect the small heats of wetting, employed a thermocouple and a galvanometer of such sensitivity that 1° change in temperature corresponded to  $1.86 \times 10^{-7}$  amp. In our opinion such investigations were not dealing with capillary adsorption at all, but were measuring the heat of adsorption on a plane surface. The initial film of adsorbed material is undoubtedly under compression, but the amount of liquid in such a state is negligible as compared with the condensation that occurs in a body exhibiting capillary structure.

It occurred to us that it might be possible to explain the above measurements from consideration of surface energy changes. Silica gel in our opinion consists of an agglomeration of silica nuclei, each particle being surrounded with an envelope of water. Therefore the gel may be regarded as exhibiting an enormous water surface which is the seat of considerable energy. When this material is immersed in water the above surface disappears due to the fact that a water-water interface cannot exist. When on the other hand, the gel is wetted by a liquid such as benzene the total surface undergoes no diminution in area, but the surface energy is greatly decreased due to the diminution of the interfacial tension. At the same time an amount of heat is set free equivalent to the decrease in surface energy, thus accounting for the heat of wetting.

Inasmuch as the total surface energy is given by the following expression

$$E = \omega \sigma - T \frac{d\sigma}{dt} \omega$$

where  $\omega$  is the surface and  $\sigma$  the surface tension, it is first necessary to ascertain whether the surface of one gram of silica gel is of sufficient magnitude to account for the measured heat effects. The surface tension of water at 25° is according to Harkins and Cheng<sup>3</sup> 72.05 dynes per cm., and the value of  $d\sigma/dt = -0.1511$ . Therefore  $E$  at 25° equals 117.08 ergs per cm<sup>2</sup>. In order to obtain a heat of wetting of 19.22 cal. per gram of gel it is necessary that the latter exhibit a surface of -

<sup>3</sup> W. D. Harkins and Y. C. Cheng, *THIS JOURNAL*, 43, 35 (1921).

$$\omega = \frac{19.22 \times 4.182 \times 10^7}{117.08} = 6.9 \times 10^6 \text{ cm.}^2$$

This figure is in good agreement with the ultra-microscopically observed degree of heterogeneity; Zsigmondy observing particles of the order of 5  $\mu\mu$  in diameter. Assuming roughly the density of the gel particles to be 2 it is evident that the surface exhibited by 1 g. of particles of the above size would be

$$\frac{3 \times 0.5}{2.5 \times 10^{-7}} = 6 \times 10^6 \text{ cm.}^2$$

It is evident from such a calculation that the surface energy is therefore sufficient to explain the observed heat effects.

There still remains to be tested the agreement between the calculated and measured values of the heat of wetting by the other liquids. In the calculation of the heat of wetting, the surface of the gel is assumed to be the same as that evaluated from the heat of wetting by water.

In the case of benzene, for example, the total surface energy after wetting is

$$E = \omega\sigma' - \omega T \frac{d\sigma'}{dt}$$

where  $\sigma'$  = the interfacial tension at the water-benzene surface. The heat of wetting by benzene is equal to the difference between the total surface energy of the gel and the above expression. Using the value given by Harkins for the free surface energy and its variation with the temperature, the total surface energy of 1 cm.<sup>2</sup> of a water-benzene interface at 25° is evaluated as 51.66 ergs per cm.<sup>2</sup>. Inasmuch as a water surface at the same temperature possesses 117.08 ergs per cm.<sup>2</sup>, it is evident that during the wetting 117.08–51.66 or 65.42 ergs per cm.<sup>2</sup> must have been converted into heat. Furthermore, if in the case of wetting by water the final surface energy was reduced to zero, then the heat of wetting by benzene should be in the ratio of 65.42:117.08 to that of the heat of wetting by water, or equal to 10.74 cal. per g. of gel. The heat of wetting observed was, 11.13 cal. per g.

In a similar manner it may be calculated using the data of Harkins that the total interfacial energy of a water-carbon tetrachloride surface at 25° is equal to 73.86 ergs per cm.<sup>2</sup>. From this value we calculated that the heat of wetting by carbon tetrachloride should be 7.10 cal. per g; the observed was 8.42 cal. per g.

In the case of aniline no data are available as to the variation of the free interfacial energy with the temperature, and evaluation of the latent surface energy is uncertain. However, we may approximate this value as follows. The interfacial tension of water-aniline at 20° is given by Harkins as 5.77 dynes per cm. The critical solution temperature of these two liquids is 167°, at which point the interfacial tension must be zero.

By assuming a straight line temperature function we therefore obtain  $d\sigma'/dt = -0.04$ . The bound surface energy at  $25^\circ$  is then found to be 11.92 ergs per  $\text{cm.}^2$  which added to the free energy gives a total surface energy of 17.69 ergs per  $\text{cm.}^2$  for the water-aniline interface. The heat of wetting by aniline may then be calculated to equal 16.56 cal. per g; the observed, was 17.54 cal. per g.

In all cases it is noted that our calculated heats of wetting are lower than the observed values, although the agreement is remarkable considering the nature of the calculations. The discrepancy is, however, easily accounted for, although unfortunately we are not able to reduce our corrections to a quantitative basis. It has been shown by Davidheiser and Patrick<sup>6</sup> that silica gel contains a certain amount of acid. Furthermore it is known that acids decrease the interfacial tension at the water-benzene boundary. In other words it is decidedly probable that the total surface energy after wetting is lower than that calculated. Furthermore it is possible that the surface energy of the gel is greater than that assumed by us, due to the fact that the adsorbed water layer exhibits a higher surface tension than does ordinary water. Both of these effects would tend to increase the heat of wetting; in our opinion, however, the lowering of the interfacial tension due to the presence of acid is sufficient to account for the entire difference between the measured and calculated values.

In the case of alcohol, at first thought we should expect the heat of wetting to be equal to the heat of wetting by water inasmuch as the water and alcohol are miscible in all proportions. The observed heat of wetting, however, is found to be 3.41 cal. per g. higher than that for water. This difference is too great to be explained on the basis of heat of solution of water in alcohol.

The ideas upon which our explanation is based will be developed in more detail in a paper under preparation dealing with the effect of capillarity upon equilibrium. Nevertheless it may be said at this time that it is conceivable that in a small capillary tube water may present a surface against alcohol. Furthermore if such a surface were to possess a positive temperature coefficient of free surface energy, we should then expect the heat of wetting by alcohol to be greater than that of water. For example the heat of wetting of silica gel by heptin may be calculated from the interfacial data of Harkins. According to the latter the total surface energy of a heptin-water surface at  $20^\circ$  equals  $-19.60$  ergs per  $\text{cm.}^2$ . We should therefore expect this liquid to exhibit a higher heat of wetting than water, namely 22.4 cal. per g. of gel.

### Summary.

1. The heats of wetting of silica gel by water, benzene, carbon tetrachloride, ethyl alcohol and aniline have been determined.

<sup>6</sup> Davidheiser and Patrick, to be published later.

2. The heat of wetting of silica gel by water has been found to be positive between  $0^{\circ}$  and  $4^{\circ}$ .

3. The observed heats of wetting have been satisfactorily accounted for on the basis of surface energy changes.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## THE TRANSFERENCE NUMBERS OF SULFURIC ACID BY THE CONCENTRATION CELL METHOD.

BY ALFRED L. FERGUSON AND WESLEY G. FRANCE.

Received June 28, 1921.

The concentration cell method for the determination of transference numbers was shown, in this laboratory<sup>1</sup> to be more accurate in the case of uni-univalent electrolytes than the Hittorf method. In the present investigation it is found to apply equally well in the case of the uni-bivalent electrolyte  $\text{H}_2\text{SO}_4$ .

The determination involves the measurement of the potentials of a concentration cell without diffusion; a concentration cell with diffusion and reversible with respect to the cation; and a concentration cell with diffusion and reversible with respect to the anion.

The total potential of the concentration cell, reversible with respect to the cation,  $\text{Pt}_\text{H} | \text{H}_2\text{SO}_4 \text{ } c_1 | \text{H}_2\text{SO}_4 \text{ } c_2 | \text{Pt}_\text{H}$ , consists of the algebraic sum of the two electrode potentials and the potential at the boundary of the solutions. On the assumption that sulfuric acid dissociates into two hydrogen ions and one sulfate ion, the algebraic sum of the electrode potentials is expressed by the well-known formula

$$E_1 = \frac{RT}{F} \ln \frac{c_1}{c_2}. \quad (1)$$

The potential at the liquid boundary is expressed by the formula

$$E_B = \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} \ln \frac{c_1}{c_2}. \quad (2)$$

The hydrogen electrode in the concentrated solution is positive with respect to the hydrogen electrode in the dilute solution. At the boundary of the solutions, the sulfuric acid diffuses from the concentrated to the dilute side, and since the hydrogen ion moves faster than the sulfate ion, the dilute side is positively charged with respect to the concentrated. This means that the potential developed at the boundary opposes the potential of the hydrogen electrodes. The total potential of the hydrogen concentration cell is, therefore, expressed by the equation

<sup>1</sup> A. L. Ferguson, *J. Phys. Chem.*, 20, 326 (1916).

$$E_1 - E_B = E_2 = \frac{RT}{F} \ln \frac{c_1}{c_2} - \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} \ln \frac{c_1}{c_2}$$

$$= \left[ 1 - \frac{2U_c - U_a}{2(U_c + U_a)} \right] \frac{RT}{F} \ln \frac{c_1}{c_2} = \frac{3}{2} \frac{U_a}{U_c + U_a} \frac{RT}{F} \ln \frac{c_1}{c_2}.$$

By the substitution of the transference number of  $N_a$ , of the anion for  $U_a/(U_a + U_c)$  the equation

$$E_H = \frac{3}{2} N_a \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (3)$$

is obtained.

The total potential of the concentration cell, reversible with respect to the anion,  $\text{Hg} | \text{Hg}_2\text{SO}_4, \text{H}_2\text{SO}_4 \text{ } c_1 | \text{H}_2\text{SO}_4 \text{ } c_2, \text{Hg}_2\text{SO}_4 | \text{Hg}$ , consists of the algebraic sum of the two electrode potentials and the potential at the boundary of the solutions. The algebraic sum of the electrode potentials is expressed by the formula

$$E_A = \frac{RT}{2F} \ln \frac{c_1}{c_2} \quad (4)$$

The boundary potential is the same as in the hydrogen concentration cell, and is in the same direction. The algebraic sum of the sulfate electrode potentials is also in this direction. Therefore the total potential of the sulfate concentration cell is expressed by the equation

$$E_A + E_B = E_{\text{SO}_4} = \frac{RT}{2F} \ln \frac{c_1}{c_2} + \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} \ln \frac{c_1}{c_2}$$

$$= \left[ \frac{1}{2} + \frac{2U_c - U_a}{2(U_c + U_a)} \right] \frac{RT}{F} \ln \frac{c_1}{c_2} = \frac{3}{2} \frac{U_c}{U_c + U_a} \frac{RT}{F} \ln \frac{c_1}{c_2}.$$

By the substitution of the transference number,  $N_c$ , of the cation for the expression  $U_c/(U_a + U_c)$  the equation becomes

$$E_{\text{SO}_4} = \frac{3}{2} N_c \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (5)$$

The potential of the concentration cell without diffusion,  $\text{Pt}_H | 0.1 \text{ } M \text{ } \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4 | \text{Hg} | \text{Hg}_2\text{SO}_4, 0.01 \text{ } M \text{ } \text{H}_2\text{SO}_4 | \text{Pt}_H$ , is represented by the equation

$$E = \frac{3}{2} \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (6)$$

The value  $E$  may be obtained experimentally from the difference between the potentials of the cells  $\text{Pt}_H | 0.1 \text{ } M \text{ } \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4 | \text{Hg}$ , and  $\text{Pt}_H | 0.01 \text{ } M \text{ } \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4 | \text{Hg}$ .

Equation 5 divided by Equation 6 gives  $E_{\text{SO}_4}/E = N_c$ , which expresses the transference number of the cation in terms of  $E_{\text{SO}_4}$  and  $E$ . In a similar way the expression  $E_H/E = N_a$ , is obtained, as  $N_a + N_c = 1$ , therefore  $E_{\text{SO}_4}/E + E_H/E = 1$ ; and

$$E_{\text{SO}_4} + E_H = E. \quad (7)$$

It is evident from Equation 7 that the same value should be obtained

by the sum of the potentials  $E_{\text{SO}_4}$  and  $E_{\text{H}}$  as by the difference of the potentials  $E_{0.01}$  and  $E_{0.1}$ .

Since, to obtain the total potential,  $E_{\text{SO}_4}$ , the boundary potential is added to the electrode potentials, while for the total potential,  $E_{\text{H}}$ , it is subtracted, then, by a combination of these as shown below, a formula is obtained which expresses the boundary potential in terms of  $E_{\text{SO}_4}$  and  $E_{\text{H}}$ .

$$\begin{aligned} E_{\text{H}} &= \frac{RT}{F} \ln \frac{c_1}{c_2} - \frac{(2-3N_a)RT}{2} \ln \frac{c_1}{c_2}; E_{\text{SO}_4} = \frac{RT}{2F} \ln \frac{c_1}{c_2} + \frac{(2-3N_a)RT}{2} \ln \frac{c_1}{c_2}; \\ 2E_{\text{SO}_4} &= \frac{RT}{F} \ln \frac{c_1}{c_2} + \frac{2(2-3N_a)RT}{2} \ln \frac{c_1}{c_2} \\ \frac{2E_{\text{SO}_4} - E_{\text{H}}}{3} &= \frac{(2-3N_a)RT}{2} \ln \frac{c_1}{c_2}. \end{aligned} \quad (8)$$

Therefore the value for the boundary potential may be obtained by the substitution of the measured potentials  $E_{\text{SO}_4}$  and  $E_{\text{H}}$  in the above equation.

### Apparatus and Materials.

The potential measurements were made with an Otto Wolff 15,000-ohm potentiometer, using a certified Weston cell as a standard. The solutions were prepared from a commercial c. p. sulfuric acid of 1.84 sp. gr. and were standardized by means of sodium carbonate prepared by the fusion of c. p. sodium hydrogen carbonate in an atmosphere of carbon dioxide. The mercurous sulfate was electrolytically prepared by the Hulett<sup>2</sup> method. The hydrogen was obtained by the electrolysis of 5 *N* sodium hydroxide solution using a generator similar to that of Bodenstein and Pohl,<sup>3</sup> and the hydrogen electrodes were of the ordinary foil type. The mercury used was twice distilled. All measurements were made with the cells contained in an electrically heated and regulated oil thermostat maintained at a constant temperature of 25°.

The concentration cell method, as previously shown, requires the consecutive measurement of 4 distinct potentials which must be extremely constant and reproducible. Much experimental work was required before the satisfactory system of cells shown in Fig. 1 was developed. In this arrangement the connections, between the separate cells, are made by means of siphons (M, N, H and G). A method whereby they could be filled with the proper solutions before being connected with the arms of the containers was considered essential. In this way new boundaries could be introduced without disturbing the electrodes. Connections were made with the cells through the reservoirs ( $R_a$ ,  $R_b$ ,  $R_c$ ,  $R_d$ , Fig. 1) on the arms of the containers.

<sup>2</sup> Hulett, *Phys. Rev.*, **32**, 257 (1911).

<sup>3</sup> Bodenstein and Pohl, *Z. Elektrochem.*, **11**, 373 (1905).



## Arrangement of Cells and Method of Procedure.

In Fig. 1, A and B are the mercurous sulfate electrodes; C and D are the hydrogen electrodes. A and C contain 0.1 *M* and B and D 0.01 *M* sulfuric acid. The electrodes A and C are connected by the siphon H, B and D by the siphon G. The two sulfate electrodes are connected by the siphon M; the two hydrogen electrodes by the siphon N.

The containers were fastened in their proper position and filled with the electrode materials. The siphons H and G were put in place and filled by suction. The stopcocks J and O, P and K were then closed. The hydrogen was admitted to C and D through the inlets S and S' and bubbled through the solutions. It escaped through the outlets W and W' into

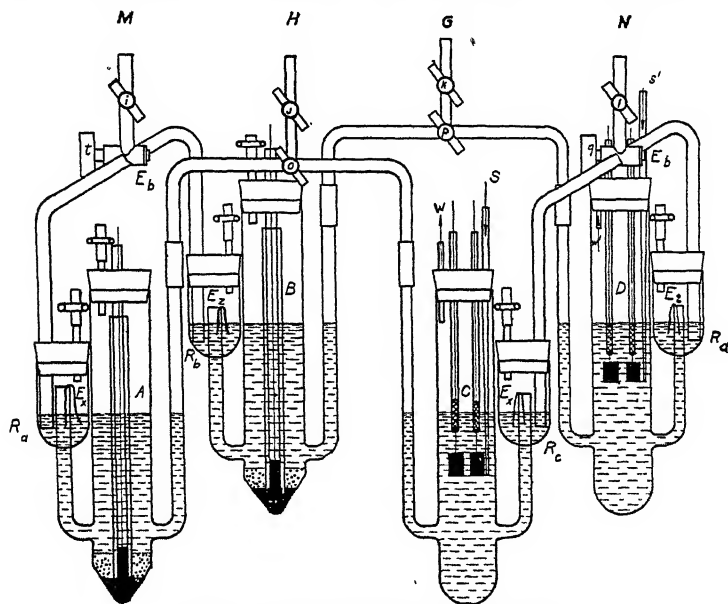


Fig. 1.—Arrangement of cells as used.

chambers (not shown) of about 10 cc. capacity. When the hydrogen electrodes became constant, the stopcock O was opened long enough to measure the potential  $E_{0.1}$  between the sulfate and hydrogen electrodes in 0.1 *M* sulfuric acid solution. In a similar way the measurement  $E_{0.01}$  was made for the sulfate and hydrogen electrodes in 0.01 *M* sulfuric acid. By the proper manipulation of the stopcocks, the solutions in those halves of siphons H and G connected to the sulfate electrodes were emptied. The arms of the siphons M and N with the rubber stoppers attached were immersed in 2 beakers which contained 0.1 *M* and 0.01 *M* sulfuric acid. The solutions were drawn into the arms of the siphons and formed the boundary within the stopcocks t and q. These siphons were then placed

in their proper positions connecting the cells.<sup>4</sup> The stopcock  $q$  was opened and the potential  $E_H$  of the hydrogen concentration cell measured. In a similar way the potential of the sulfate concentration cell ( $E_{SO_4}$ ) was measured.

The leads from the electrodes were permanently connected to a switch-board so the potentials between any two electrodes could be measured by the manipulation of a switch connected to the potentiometer.

In the first part of the work the measurements showed considerable fluctuation, which was traced to the leakage of current from the high potential electrical circuits in connection with the thermostat. The difficulty was overcome by the replacement of the water by kerosene.

During the development of this work some information was obtained which may be of assistance to others concerned with similar investigations. It was found that the length of time required for the mercurous sulfate electrodes to reach a condition of equilibrium could be greatly reduced by vigorously shaking the sulfuric acid and mercurous sulfate in a mechanical shaker before using in the cells. The first cells constructed contained the hydrogen electrodes in the same chamber as the mercurous sulfate electrode and the potentials were found to vary greatly. This was believed to be due to the catalytic effect of the platinum black which was loosened by the action of the hydrogen on the electrode and fell on to the mercurous sulfate. The difficulty was eliminated by the use of separate chambers for the electrodes.

The final measurements were made and are given in four tables of which I and II are examples.

In the following tables Col.  $E_H$  contains the potentials of the hydrogen concentration cell with diffusion,  $Pt_H | 0.1 M H_2SO_4 | 0.01 M H_2SO_4 | Pt_H$ ;

TABLE I.

No.	Date.	Time.	Bar. Mm.	$E_H$	$E_{SO_4}$	$E_{0.1}$	$E_{0.01}$	$\frac{E}{E_H + E_{SO_4}}$ by $E_{0.01}$	$\frac{E}{E_{0.1}}$ by $E_{0.01}$
1	10/13	3:00 P.M.	741.6	.....	.....	0.74202	0.80260	.....	.....
2	10/13	4:00	741.6	.....	.....	0.74200	0.80260	.....	.....
3	10/13	7:30	740.4	0.01137	0.04933	0.74205	0.80275	0.06070	0.06070
4	10/13	9:00	740.0	0.01139	0.04930	0.74210	0.80274	0.06069	0.06064
5	10/13	10:30	740.0	0.01139	0.04929	0.74212	0.80276	0.06068	0.06064
6	10/13	11:30	739.5	0.01141	0.04928	0.74212	0.80279	0.06069	0.06067
7	10/14	10:00 A.M.	736.0	0.01136	0.04900	0.74203	0.80249	0.06036	0.06036
8	10/14	1:30 P.M.	734.5	0.01133	0.04913	0.74201	0.80246	0.06046	0.06035
9	10/14	3:30	734.5	0.01130	0.04918	0.74203	0.80245	0.06048	0.06042
Av.				0.01136	0.04922	0.74207	0.80263	0.06058	0.06056

The cell was set up at 9:00 A.M. on October 13, 1919.

<sup>4</sup> In the measurement for the transference numbers of  $H_2SO_4$  the reservoirs ( $R_a$ ,  $R_b$ ,  $R_c$ ,  $R_d$ ) were filled above the openings of the side arms. In the later work when gelatin was used they were filled as shown in the diagram.

TABLE II.

1	10/15	10:00 A.M.	739.3	.....	.....	0.74166	0.80192	.....	.....
2	10/15	1:30 P.M.	.....	.....	.....	0.74209	0.80263	.....	.....
3	10/15	5:45	.....	.....	.....	0.74200	0.80268	.....	.....
4	10/15	7:15	.....	.....	.....	0.74205	0.80269	.....	.....
5	10/15	10:00	737.3	0.01136	0.04922	0.74195	0.80256	0.06058	0.06061
6	10/15	12:00	737.0	0.01127	0.04921	0.74212	0.80257	0.06048	0.06045
7	10/16	9:00 A.M.	736.3	0.01120	0.04927	0.74209	0.80253	0.06047	0.06044
8	10/16	10:30	736.5	0.01121	0.04923	0.74210	0.80247	0.06044	0.06037
Av.			0.01126	0.04923	0.74206	0.80253	0.06049	0.06047	

The cell was set up at 11 P.M. on October 14, 1919.

Col.  $E_{\text{SO}_4}$  those of the sulfate concentration cell with diffusion,  $\text{Hg} | \text{Hg}_2\text{SO}_4$  0.01  $M$   $\text{H}_2\text{SO}_4$  | 0.1  $M$   $\text{H}_2\text{SO}_4$ ,  $\text{Hg}_2\text{SO}_4 | \text{Hg}$ ; Col.  $E_{0.1}$  the potentials of the cell,  $\text{Pt}_\text{H} | 0.1 M \text{H}_2\text{SO}_4$ ,  $\text{Hg}_2\text{SO}_4 | \text{Hg}$ ; and Col.  $E_{0.01}$  the potentials of the cell,  $\text{Pt}_\text{H} | 0.01 M \text{H}_2\text{SO}_4$ ,  $\text{Hg}_2\text{SO}_4 | \text{Hg}$ . The column headed " $E$  by  $E_\text{H} + E_{\text{SO}_4}$ " contains the sums of the values recorded in Cols.  $E_\text{H}$  and  $E_{\text{SO}_4}$ . The column " $E$  by  $E_{0.01} - E_{0.1}$ " contains the differences between the values recorded in  $E_{0.01}$  and  $E_{0.1}$ .

The 0.1  $M$  and 0.01  $M$  cells were prepared and placed in the thermostat where they remained for about 12 hours to come to equilibrium before the boundaries were introduced. This accounts for the blank spaces in the tables.

As pointed out in the theoretical discussion the values recorded in column  $E_\text{H} + E_{\text{SO}_4}$  should be equal to those recorded in column  $E_{0.01} - E_{0.1}$ . The close agreement of these values indicates the accuracy of the potential measurements. The differences between the successive values in each column indicates the degree of constancy of the cells. The differences in columns  $E_{0.01}$  and  $E_{0.1}$  may be attributed, in part, to changes in barometric pressure, for which corrections have not been applied, as such corrections are unnecessary for the calculations in which the measurements are used.

The remarkable agreement between the averages in the different tables indicates the reproducibility of the work.

In the theoretical treatment formulas were given by means of which the values of  $E$ ,  $E_\text{H}$ ,  $E_{\text{SO}_4}$  and  $E_\text{B}$  can be calculated. Table III contains a summary of such calculated values together with the measured values.

TABLE III.—COMPARISON BETWEEN CALCULATED AND MEASURED POTENTIALS.

	$E'$ .	$E''$ .	$E$ .	$E_\text{H}$ .	$E_{\text{SO}_4}$ .	$E_\text{B}$ .
Calc. from { Cond.	0.10511	0.06693	0.07883	0.014716	0.06407	0.03781
{ Fz. Pt.	0.08072	.....	0.06054	0.011301	0.04918	0.02908
Measured	.....	.....	0.06054	0.011310	0.04925	0.02906

These calculations involve the ratio  $\alpha_1 C_1 / \alpha_2 C_2$ . It has been customary to use conductivity values in its calculation: Since the work of Jones

is probably the most reliable on the conductivity of sulfuric acid, his results were used in these calculations. This ratio may also be obtained from freezing-point data. The values obtained from these two sources are decidedly at variance. No freezing-point data are available for the degree of dissociation of 0.1 *M* sulfuric acid. However, a complete table is given by Lewis and Linhart<sup>5</sup> for concentrations between  $10^{-2}$  and  $10^{-6}$  molar. The degree of dissociation given by Lewis and Linhart for 0.01 *M* sulfuric acid was substituted in the equation for *E* together with the measured potential (0.06054), and the equation solved for the degree of dissociation for 0.1 *M* sulfuric acid. In the curve of Fig. 2

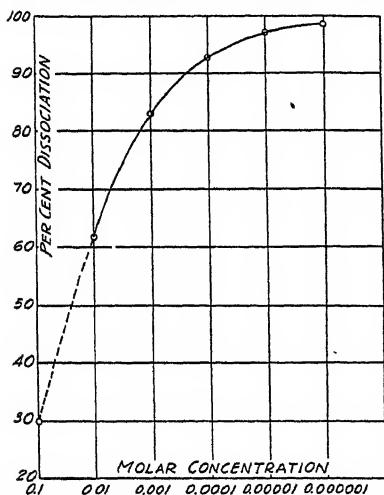


Fig. 2.—Dissociation-concentration curve.

the abscissas are the molar concentrations and the ordinates the degrees of dissociation. The portion indicated by the solid line was obtained from the freezing-point data and the broken portion is an extension to include the value calculated from the potential measurements. Since this is a smooth curve, the indication is that the point obtained from the potential measurements is approximately the same as would have been obtained from the freezing-point determination. In every instance the results obtained when the freezing-point values are used in the ratio  $\alpha_1 C_1 / \alpha_2 C_2$  show better agreement with the measured potentials than when the conductivity values are used. The latter results are in all cases higher than the measured. It should be noticed,

however, that the exact agreement between the measured and calculated values for *E* is to be expected, since it was from this measured value of *E* that  $C_2$  was calculated. The close agreement between the measured and calculated values of  $E_H$ ,  $E_{SO_4}$ , and  $E_B$  is a true indication of the correctness of the value 0.2973 for the degree of dissociation of 0.1 *M* sulfuric acid.

<sup>5</sup> Lewis and Linhart, *THIS JOURNAL*, 41, 1959 (1919).

the sulfuric acid dissociates almost entirely into 3 ions at these concentrations.

It has been noticed by others that the calculated values for potential measurements are always higher than the measured values when conductivity dissociation ratios are used. Ferguson<sup>1</sup> in his work on hydrochloric acid attributed the difference to the fact that the formula assumes the complete dissociation of the acid. As the acid is not completely dissociated the formula does not exactly represent the facts and must be corrected so as to include the undissociated acid. Such a correction was made for hydrochloric acid and, when applied to the formulas involving conductivity ratios, gave values which agreed more closely with those measured. A similar correction can be developed for the sulfuric acid concentration cell.

When two faradays of electricity pass through a sulfuric acid concentration double cell, one mol of acid is transferred from one concentration to the other. The electrical work which accompanies this change is represented by  $W = 2 EF$ . The osmotic work required to effect this same change is usually represented by  $W = 3 RT \ln c_1/c_2$ . This assumes that the acid is completely dissociated into 3 ions. Since it is not completely dissociated what actually happens is (1) the transference of an amount of hydrogen ion equal to twice the concentration times the dissociation of the acid; (2) the transference of an amount of sulfate ion equal to the concentration times the dissociation of the acid; (3) the transference of an amount of undissociated acid equal to the concentration of the undissociated acid. The general expression which represents the sum of the osmotic work in (1) and (2) is  $W_1 = \alpha 3RT \ln \frac{c_1}{c_2}$ .

Similarly the osmotic work in (3) is  $W = (1-\alpha)RT \ln \frac{c_1}{c_2}$ . In the application to sulfuric acid ( $c_1$ ) in ( $W_1$ ) becomes  $2c_1H^+ = 2c_1\alpha' = c_1SO_4^{--}$ ; and  $c_2$  becomes  $2c_2H^+ = 2c_2\alpha'' = c_2SO_4^{--}$ .

Similarly  $c_1$  in  $W_2$  becomes  $c_1H_2SO_4 = c_1(1-\alpha')$ ; and  $c_2$  becomes  $c_2H_2SO_4 = c_2(1-\alpha'')$ ; and, as the total electrical work is equal to the total osmotic work,

$$W = 2EF = \alpha 3RT \ln \frac{c_1\alpha'}{c_2\alpha''} + (1-\alpha) RT \ln \frac{c_1(1-\alpha')}{c_2(1-\alpha'')}$$

$$E = \alpha \frac{3}{2} \frac{RT}{F} \ln \frac{c_1\alpha'}{c_2\alpha''} + \frac{(1-\alpha)}{2} \frac{RT}{F} \ln \frac{c_1(1-\alpha')}{c_2(1-\alpha'')}$$

This formula cannot be taken as absolutely correct since it assumes that the dissociation is the same in both concentrations, which is not true.

The most reliable value that can be used for  $\alpha$  is  $\frac{\alpha' + \alpha''}{2}$ , in which  $\alpha$  is the degree of dissociation in  $c_1$  and  $\alpha''$  is the degree of dissociation in  $c_2$ .

Col.  $E''$  Table III shows the result of the application of this correction. It is evident that the correction is an improvement since the difference (0.00639) between the measured value and that calculated from the corrected formula is much less than the difference (0.01829) between the measured value and that calculated from the usual formula.

In the theoretical part of this work it was shown that the boundary potential can be calculated from the formula  $E_B = \frac{2-3}{2} \frac{N_a}{F} \frac{RT}{F} \ln \frac{c_1}{c_2}$ , also that  $E_B = \frac{2E_{\text{SO}_4} - E_H}{3}$ . Column  $E_B$  contains the results from the calculation by the first formula. Again the close agreement between the measured and calculated values in the case of the freezing-point ratio and lack of agreement in the case of the conductivity ratio are evident.

MacInnes<sup>6</sup> has developed a formula for boundary potentials of uni-univalent electrolytes which involves the transference number of the cation and the potentials of the cells with and without diffusion. He states that it "contains no assumption regarding the concentration of the ions of the solutions." In the following development the same reasoning is applied to the uni-bivalent acid, sulfuric acid, on the assumption that it dissociates into two hydrogen ions and one sulfate ion.

When two faradays of electricity pass through the cell the net result is the transference of one mol of sulfuric acid from the concentrated to the dilute side. The current is carried across the boundary between the two solutions by the transference of  $2N_c$  gram ions of hydrogen ions in one direction and  $1 - N_c$  gram ions of sulfate ions in the opposite. The osmotic work at the boundary is proportional to the algebraic sum of the number of gram ions that have passed through it. Therefore the osmotic work  $W$  is proportional to  $3N_c - 1$ . The electrical work which accompanies the transference of one mol of sulfuric acid from the concentrated to the dilute side is equal to the product of the electromotive force of the cell and the number of faradays required to effect the transference. Since this is so, the following relation holds.

$$2EF:2E_B F::3:3N_c-1$$

and  $E_B = E(3N_c - 1)/3$ ; for  $E$ ,  $\frac{E_{\text{SO}_4}}{N_c}$  may be substituted, since it has been shown that  $N_c = \frac{E_{\text{SO}_4}}{E}$ . The formula then becomes

$$E_B = E_{\text{SO}_4} (3N_c - 1) / 3N_c.$$

Substituting the correct values for  $N_c$  and  $E_{\text{SO}_4}$  as measured, the value 0.02904 is obtained. This is in almost perfect agreement with the measured value 0.02906 and proves the validity of the formula.

<sup>6</sup> MacInnes, *THIS JOURNAL*, 37, 2301 (1915).

That this expression  $E_B = E_{\text{SO}_4} (3N_c - 1) / 3N_c$  is but another form of the usual expression  $E_B = \frac{2-3N_a}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}$  for boundary potential, can readily be shown, since

$$E_B = \frac{E_{\text{SO}_4}}{3N_c} (3N_c - 1) \quad (9)$$

and

$$E_{\text{SO}_4} = N_c \frac{3}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}.$$

Substituting in (9)

$$E_B = \frac{N_c \frac{3}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}}{3N_c} (3N_c - 1) = \frac{RT}{F} \ln \frac{c_2}{c_1} (3N_c - 1)$$

is obtained; as  $(3N_c - 1) = (2 - 3N_a)$

$$E_B = \frac{RT}{F} \ln \frac{c_1}{c_2} (3N_c - 1) = \frac{2 - 3N_a}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}.$$

Therefore

$$E_B = \frac{E_{\text{SO}_4}}{3N_c} (3N_c - 1) = \frac{2 - 3N_a}{2} \frac{RT}{F} \ln \frac{c_1}{c_2} = \frac{2E_{\text{SO}_4} - E_H}{3}.$$

A consideration of these formulas indicates the advantage of the formula  $(2E_{\text{SO}_4} - E_H)/3$  since it contains no assumption regarding the concentration of the ions, nor does it require a knowledge of the transference numbers.

The averages of  $E_H$ ,  $E_{\text{SO}_4}$ , and  $E$  from a few of the tables obtained are contained in Table IV, together with the transference numbers calculated from them.

TABLE IV.  
SUMMARY OF POTENTIALS AND TRANSFERENCE NUMBERS.

Table.	$E_H$ .	$E_{\text{SO}_4}$	$\frac{E \text{ or } E_{0.01}-E_{0.1}}{E_{0.01}-E_{0.1}}$	$\frac{N_a}{E_H/E}$	$\frac{N_a}{1-E_{\text{SO}_4}/E}$
II	0.01136	0.04922	0.06056	0.1875	0.1875
III	0.01126	0.04923	0.06047	0.1862	0.1862
IV	0.01137	0.04929	0.06059	0.1875	0.1874
V	0.01126	0.04927	0.06053	0.1868	0.1868
Av.	0.01131	0.04925	0.06054	0.1868	0.1868

To facilitate the comparison of the value obtained in this investigation with those obtained in others, a summary of such values is contained in Table V.

Attention should be called to the fact that the values recorded in columns  $E_H/E$  and  $1 - E_{\text{SO}_4}/E$  of Table IV are determined from separate and distinct potential measurements. The agreement between the successive values in each column and between the averages of the two columns demonstrates the reliability of the concentration cell method for the determination of the transference numbers of sulfuric acid.

TABLE V.  
SUMMARY OF TRANSFERENCE NUMBERS OF SULFURIC ACID.

Investigator. <sup>1</sup>		Concentration.	Temp. ° C.	$N_g$ .	$N_g$ corrected to 25°.
Bein	1898	0.24%	11	0.175 $\pm$ 3	0.1804
McIntosh	1898	1.0—0.001 <i>M</i>	18	0.174 $\pm$ 18	0.1817
Starck	1899	0.5—0.6%	17—20	0.145 $\pm$ 7	.....
Jahn and Huybrechts	1902	0.06—0.005 <i>M</i>	18	0.176 $\pm$ 4	0.1837
Eisenstein	1902	0.124 <i>M</i>	18	0.168 $\pm$ 3	0.1757
Eisenstein	1902	0.01 <i>M</i>	30	0.188 $\pm$ 1	0.1825
Tower	1904	0.1 <i>M</i>	20	0.1805	0.1860
Tower	1904	0.01 <i>M</i>	20	0.1809	0.1864
Whetham and Paine	1908	0.05 <i>M</i>	18	0.184	0.1917
Ferguson and France	1920	0.1—0.01 <i>M</i>	25	0.1868	0.1868

### Summary.

1. A method has been described for the determination of the transference numbers of a uni-bivalent electrolyte by the measurement of the potentials of concentration cells.

2. The transference number of the anion of sulfuric acid for concentrations between 0.1 *M* and 0.01 *M* has been measured and found to be  $0.1868 \pm 7$  at 25°.

3. It has been shown that dissociation values determined from freezing-point data are more satisfactory for calculating the potentials of concentration cells than those obtained from conductivity data.

4. A correction to the formula for the potential of a concentration cell has been developed which takes into account the undissociated part of the acid.

5. It has been shown that the concentration-cell method is entirely satisfactory for the determination of the transference numbers of sulfuric acid.

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<sup>1</sup> The values and the limits of accuracy of the first six investigations are taken from MacBain's abstract of transference data (*J. Wash. Acad. Sci.*, 9, 11 (1905)). In the first six investigations the analytical method was employed. According to MacBain the results of Jahn and Huybrechts and of Tower are probably the most reliable. Whetham and Paine employed the conductivity method. The values in the last column were obtained from the values in the preceding column by the application of the temperature coefficients given by Tower (*THIS JOURNAL*, 26, 1038 (1904)).



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## THE INFLUENCE OF GELATIN ON THE TRANSFERENCE NUMBERS OF SULFURIC ACID.

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Received June 28, 1921.

The properties of hydrophile colloids have been the subject of many investigations during the past few years. So far, no entirely satisfactory explanation has been offered for their action in the presence of electrolytes. The theories advanced are based largely on the measurements of osmotic pressure, conductivity, swelling and transference numbers.

There appear to be but three articles in the literature dealing with the influence of colloids on transference numbers and in each instance the analytical method was used.

Paul Richter<sup>1</sup> investigated the influence of gelatin, gum arabic, agar-agar, and peptone on the transference number of the chloride ion of lithium, potassium and hydrogen chlorides.

A. Mutscheller<sup>2</sup> investigated the influence of gelatin on the transference numbers of silver nitrate, cupric sulfate and zinc sulfate solutions which contained definite quantities of a 1% gelatin solution.

According to his results the transference numbers of the nitrate and sulfate ions decrease with an increase in the quantity of gelatin solution added. By the addition of sufficient quantities of gelatin solution, even negative values were obtained. He states that when the transference number of the anion is zero the conditions are most favorable for the deposition of the metal. The effect of the gelatin is accounted for on the assumption that it is positively charged and forms an "absorption compound" with the anions. This results in the partial or complete neutralization or even reversal of the original charge on the ions. The results obtained by Mutscheller for the sulfate and nitrate ions show effects of gelatin far in excess of those observed by Richter for the chloride ion.

It is well to emphasize here that the results obtained by Mutscheller, if correct, are indeed remarkable, but it is the opinion of the authors that an error has been made in the calculations or in the recorded data. This subject is under investigation at the present time.

In an earlier article<sup>3</sup> the authors described in detail the application of the concentration cell method to the determination of the transference numbers of sulfuric acid and demonstrated its reliability. The method lends itself admirably to the determination of the influence of gelatin on the transference numbers of sulfuric acid. In that article it was also

<sup>1</sup> Richter, *Z. physik. Chem.*, **80**, 449 (1912).

<sup>2</sup> Mutscheller, *Met. Chem. Eng.*, **13**, 353 (1915); *THIS JOURNAL*, **42**, 442 (1920).

<sup>3</sup> Ferguson and France, *THIS JOURNAL*, **43**, 2150 (1921).

pointed out that the boundary potential is an important factor in the determination of transference numbers by the concentration-cell method.

Mutscheller<sup>2</sup> explains the effect of gelatin on the transference numbers of silver nitrate, cupric sulfate and zinc sulfate by the assumption that gelatin is positively charged and "absorbs" the negative ions. This causes a decrease in their velocity. According to Nernst the potential at the boundary of two solutions of different concentration depends upon the difference in velocities of the ions. If the theory of Mutscheller is true the presence of gelatin in such solutions should change the boundary potential. Then measurements of the transference numbers of sulfuric acid by this method would determine whether gelatin affected the boundary potential.

Since gelatin precipitates the heavy metals, it was obvious that precipitation would result if it were added to a sulfuric acid solution saturated with mercurous sulfate. Since, however, the influence of the gelatin on transference numbers is due only to its effect on the boundary potential, it is unnecessary to introduce gelatin into the electrode containers.

The cells were prepared as described in the previous article and the siphons connecting the hydrogen and sulfate electrodes were filled with 0.1 *M* and 0.01 *M* solutions of sulfuric acid which contained a definite concentration of gelatin. They were then placed in the reservoirs, with the ends immersed in solutions of the same concentration as that which surrounded the electrodes.

The measurements were made as before, but showed a gradual progressive change. It was discovered that this was due to the diffusion of the gelatin from the siphons into the reservoirs and then into the solution which surrounded the electrodes. This made it necessary to devise a method which would prevent the diffusion and at the same time introduce no new potentials. Several devices were tried in which use was made of glass wool, filter paper, glass capillaries, and cotton wicks, before the following satisfactory method was found.

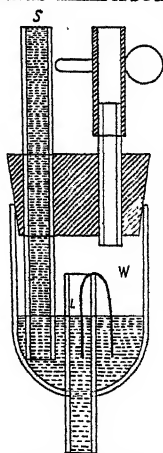


Fig. 1.—Detail of reservoir.

and so filled that the solution rose in the inner tube to the level *L*, indicated in Fig. 1. Gelatin solution identical with that in the siphon *S* was filled in the reservoirs to the level *L*. A wick *W* previously saturated with acid solution containing no gelatin was hung over the side of the inner tube so that one end of it was immersed in the plain solution of the inner tube and the other in the gelatin solution in the reservoir. This arrangement effectively eliminated the

diffusion, provided the solutions in the inner tube and in the reservoir were maintained at the same level. No new potentials were introduced by this arrangement. All of the measurements were made with cells prepared in this manner. Measurements were made with concentrations of gelatin over a range of 0.5 to 20.0%. The results of these measurements are contained in 18 tables of which Table I is a sample.

TABLE I.—TYPICAL EXPERIMENTS.

Expt. Date.	Time.	Bar.	$E_H$	$E_{SO_4}$	$E_{0.1}$	$E_{.01}$	$E_{\text{by } E_H + E_{SO_4}}$	$E_{\text{by } E_{.01} - E_{0.1}}$
		Mm.	Using 0.5% gelatin.					
1	1/24 12:30 A.M.	743.8	.....	.....	0.74189	0.80260	.....	.....
2	1/24 9:30	748.4	.....	.....	0.74205	0.80264	.....	.....
3	1/24 11:50	748.4	.....	.....	0.74203	0.80260	.....	.....
Using 5% gelatin siphons introduced at 1 P.M.								
4	1/24 1:00 P.M.	747.8	0.01295	0.04750	0.74199	0.80235	.....	.....
5	1/24 5:00	749.6	0.01290	0.04743	0.74210	0.80220	0.06033	0.06010
6	1/24 11:00	751.0	0.01292	0.04740	0.74217	0.80237	0.06032	0.06020
7	1/25 10:30 A.M.	754.2	0.01290	0.04779	0.74213	0.80260	0.06069	0.06047
	Av.		0.01290	0.04754	0.74213	0.80239	0.06044	0.06026

The cell was set up on Jan. 23 at 2:30 P.M. The averages do not include the first four sets of readings.

In these tables the same arrangement of the data has been followed as in the previous article. In order that a comparison of the values recorded in the separate tables may readily be made, the average values in each table together with the transference numbers calculated therefrom have been summarized in Table II.

The headings of Cols. 2, 3, 4, and 5 have the same significance as in the previous article. Cols. 6, 7, 8, and 9 contain the transference numbers calculated from the values in Cols. 2, 3, 4, and 5, as indicated in the headings. Col. 10 contains the sum of the  $N_a$  and  $N_c$  values of Cols. 7 and 9 and should always be equal to unity. The deviation from unity is an indication of the small error of the potentials used in their calculation. The accuracy with which the potentials of  $E_H$  and  $S_{SO_4}$  can be duplicated in the presence of gelatin, is shown by the closeness with which the averages for any two tables of the same concentration agree. From a comparison with similar values in the tables of the previous article, it is plainly evident that when gelatin is present the agreement is less satisfactory than when it is not. This lack of agreement becomes greater the higher the concentration of gelatin. Table III is a summary of the averages of the potentials and transference numbers contained in Table II.

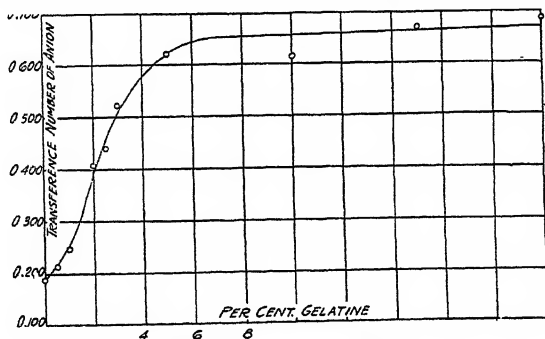
TABLE II.—SUMMARY OF POTENTIALS AND TRANSPERANCE NUMBERS WITH GELATIN.

1. Table.	2. $E_H$	3. $E_{\text{sol}}$	4. $\frac{E_H + E_{\text{sol}}}{E_{\text{sol}}}$	5. $\frac{E_{0.01} - E_{0.1}}{E_{0.1}}$	6. $\frac{N_a}{E_H + E_{\text{sol}}}$	7. $\frac{N_a}{E_H}$	8. $\frac{N_c}{E_{\text{sol}}}$	9. $\frac{N_c}{E_{0.01} - E_{0.1}}$	10. $\frac{N_a + N_c}{\text{Cols. 7 + 9.}}$
Average from previous article.	0.01131	0.04925	0.06056	0%	0.1868	1.0868	0.8133	0.8135	1.0001
IX	0.01290	0.04754	0.06044	0.5%	0.213	0.214	0.786	0.789	1.003
Av.	0.01289	0.04774	0.06063	0.06049	0.213	0.213	0.787	0.789	1.002
XI	0.01480	0.04549	0.06029	1.0%	0.246	0.245	0.754	0.753	0.998
XII	0.01507	0.04577	0.06084	0.06070	0.248	0.248	0.752	0.754	1.002
Av.	0.01494	0.04563	0.06056	0.06055	0.247	0.247	0.753	0.754	1.000
XIII	0.02476	0.03799	0.06275	2.0%	0.395	0.407	0.605	0.625	1.033
XIV	0.02466	0.03699	0.06165	0.06067	0.400	0.407	0.600	0.610	1.010
Av.	0.02471	0.03749	0.06220	0.06072	0.397	0.407	0.603	0.617	1.025
XV	0.02703	0.03213	0.05921	2.5%	0.457	0.445	0.543	0.528	0.974
XVI	0.02655	0.03239	0.05894	0.06064	0.450	0.438	0.550	0.534	0.972
Av.	0.02682	0.03266	0.05907	0.06072	0.453	0.442	0.547	0.531	0.973
XVII	0.03062	0.02809	0.05871	3.0%	0.521	0.503	0.478	0.461	0.964
XVIII	0.03300	0.02839	0.06139	0.06065	0.537	0.544	0.462	0.467	1.011
Av.	0.03181	0.02824	0.06005	0.06075	0.529	0.524	0.470	0.464	0.987
XIX	0.03838	0.02278	0.06106	5.0%	0.627	0.632	0.373	0.376	1.008
XX	0.03683	0.02539	0.06222	0.06059	0.592	0.607	0.408	0.419	1.026
Av.	0.03755	0.02408	0.06169	0.06069	0.610	0.620	0.390	0.398	1.017
XXI	0.03814	0.02406	0.06220	10.0%	0.613	0.625	0.387	0.397	1.000
XXII	0.03655	0.02414	0.06069	0.06085	0.602	0.601	0.398	0.397	0.997
Av.	0.03735	0.02410	0.06145	0.06092	0.608	0.613	0.393	0.397	0.999
XXIII	0.04041	0.02267	0.06308	15.0%	0.641	0.664	0.359	0.373	1.037
XXIV	0.04088	0.02219	0.06307	0.06076	0.648	0.673	0.352	0.305	1.038
Av.	0.04065	0.02243	0.06308	0.06081	0.645	0.669	0.356	0.369	1.038
XXV	0.04117	0.02057	0.06174	20.0%	0.667	0.678	0.333	0.359	1.017
XXVI	0.04194	0.02078	0.06272	0.06071	0.669	0.691	0.331	0.342	1.033
Av.	0.04157	0.02068	0.06223	0.06073	0.668	0.685	0.332	0.341	1.025

TABLE III.—SUMMARY OF POTENTIALS AND TRANSFERENCE NUMBERS.

% Gel.	$E_H$ .	$E_{SO_4}$ .	$N_a$ .	$E_B$ .
0.0	0.01136	0.04918	0.187	0.02906
0.5	0.01290	0.04784	0.213	0.02746
1.0	0.01494	0.04563	0.247	0.02544
2.0	0.02741	0.03749	0.407	0.01676
2.5	0.02682	0.03266	0.442	0.01283
3.0	0.03181	0.02824	0.524	0.00822
5.0	0.03755	0.02408	0.620	0.00354
10.0	0.03735	0.02410	0.613	0.00362
15.0	0.04065	0.02243	0.668	0.00140
20.0	0.04155	0.02068	0.685	-0.00006

A consideration of the values recorded for  $N_a$  shows that they increase with increase in concentration of gelatin. The relation between the transference number of the anion and concentration of gelatin is shown by the curve in Fig. 2. In this curve the transference numbers are plotted as

Fig. 2.— $N_a$ -gelatin curve.

ordinates and the concentrations of gelatin as abscissas. The change in transference number with increase in gelatin is rapid at low gelatin concentrations, is gradual between 3 and 5%, and above this is not appreciable. If this represents an actual increase in the migration velocity of the anion, then there must be a corresponding decrease in the boundary potential ( $E_B$ ). The values in the columns headed  $E_B$  and  $N_a$  indicate such changes. Since the boundary potential is opposed to the electrode potentials in the case of the hydrogen concentration cell ( $E_H$ ) and is added to the electrode potentials in the case of the sulfate concentration cell ( $E_{SO_4}$ ) a decrease in  $E_B$  would result in an increase in the value of  $E_H$  and a decrease in  $E_{SO_4}$ . That such changes do take place is indicated by the values in the columns headed  $E_H$  and  $E_{SO_4}$ .

It has been shown that the boundary potential depends on the transference numbers of the ions and the ratio of their concentrations in the two solutions. Therefore a change in  $E_B$  would result from a change in concentration or a change in transference number.

The value of  $E_B$  would be reduced by making the concentration of the solutions more nearly equal. When exactly equal  $E_B$  would be zero, and when the concentration of the 0.1  $M$  solution became less than that of the 0.01  $M$ , the direction would be reversed.

To determine whether or not concentration changes are produced by the gelatin, concentration cells of the type  $\text{Pt}_H | 0.1 \text{ } M \text{ } H_2SO_4 | \text{KCl} | 0.1 \text{ } M \text{ } H_2SO_4 + \text{gel.} | \text{Pt}_H$  and  $\text{Pt}_H | 0.01 \text{ } M \text{ } H_2SO_4 | \text{KCl} | 0.01 \text{ } M \text{ } H_2SO_4 + \text{gel.} | \text{Pt}_H$  were used. The data from these measurements are summarized in Table IV.

TABLE IV.

% Gel.	0.1 $M$ .		0.01 $M$ .	
	$C_1$	$E_x$	$C_2$	$E_z$
0	0.05946	.....	0.012340	.....
1	0.05694	0.00070	0.007684	0.01216
2	0.05670	0.00122	0.002172	0.04458
3	0.05542	0.00181	0.000430.	0.08609
4	0.05356	0.00268	0.000144	0.11418

It was impossible to work with concentrations of gelatin above 4% because of the excessive foaming of the solutions.

The first column contains the percentage of gelatin in the acid in one-half of the cell. The columns  $E_x$  and  $E_z$  contain the measured potentials of the cells  $E_x$  and  $E_z$  when 0.1  $M$  and 0.01  $M$  solutions are used. In columns  $C_1$  and  $C_2$  are the hydrogen-ion concentrations in 0.1  $M$  and 0.01  $M$  solutions with gelatin, calculated by the use of the formula for concentration cells in which boundary potential has been eliminated. The results in columns  $C_1$  and  $C_2$  show that gelatin produces a relatively small decrease in the hydrogen-ion concentration of the 0.1  $M$  solution, and a much greater relative decrease in the 0.01  $M$  solution. The hydrogen-ion concentration of the 0.1  $M$  solution is always greater than that of the 0.01  $M$ ; therefore the reversal of the boundary potential ( $E_B$ ) as shown in Table II cannot result from the concentration changes produced by the gelatin. Since  $E_B$  can be decreased or reversed only by a change in concentration or transference number, the observed change must be due to a change in the transference number.

Since it has been shown above that the gelatin produces changes in the hydrogen-ion concentration, new potentials are developed at the boundaries between the solutions in the wicks and the gelatin solution in the reservoirs. The locations and directions of the boundary potentials,  $E_B$ ,  $E_x$ , and  $E_z$  together with  $E_H$  and  $E_{SO_4}$  are represented diagrammatically in Fig. 3. The location of the boundary potentials is shown also by the same letters in Fig. 1 of the previous article.  $E_B$  represents the potential within the siphon, that is, the potential which has been considered thus far.  $E_x$  and  $E_z$  represent the potentials at the contact of the solutions in the reservoirs.  $E_H$  and  $E_{SO_4}$  are the measured potentials and are the

algebraic sums of the potentials at the electrodes and the boundary potentials  $E_x$ ,  $E_B$ , and  $E_z$ .

The potentials  $E_x$ ,  $E_B$ , and  $E_z$  which result from the presence of the gelatin can be calculated from the data in Table IV by the use of the usual formula for boundary potential. These calculations were made and the results are included in Table V. The potentials at  $E_x$  and  $E_z$  are oppositely directed and the resultant potential is therefore their difference. These differences are recorded in the column headed  $E_z - E_x$ . The total potential at  $E_B$  is opposed to the resultant potentials  $E_z - E_x$  and may be considered as the sum of the original boundary potential  $E_B$  (0.02906) and the potential resulting from the changes in concentration produced by the gelatin. Therefore the differences between the total potentials  $E'_B$  and the original potential  $E_B$  (0.02906) is that due to the changes in concentration produced by the gelatin. The values of these differences are recorded in the column headed  $E'_B - 0.02906$ . As the values in the column headed  $E'_B - 0.02906$  are practically identical with those in  $E_z - E_x$  and oppositely directed, their combined effect must be zero. This shows that the potentials  $E_x$  and  $E_z$  at the contacts between the solutions in the wicks and the gelatin solutions in the reservoirs are entirely compensated by the potential ( $E'_B - 0.02906$ ) simultaneously developed at the boundary  $E_B$ . Therefore any boundary potential produced by the introduction of gelatin cannot result from changes in concentration. The experimental data, however, show that the boundary potential  $E_B$  is changed by the addition of gelatin. Since this cannot be due to concentration changes it must result from a change in the transference numbers of the hydrogen and sulfate ions or from an actual change in the kind of ions present. This may be effected in several ways; (1) by the removal of either ion as the result of its being selectively adsorbed by the gelatin; (2) by a change in the velocity of either ion; (3) by chemical reaction with the gelatin resulting in the formation of new ions.

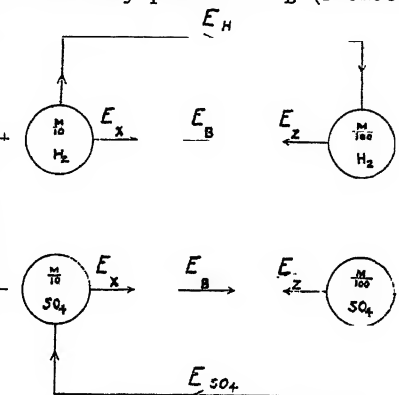


Fig. 3.—Diagram of potentials.

TABLE V.—BOUNDARY POTENTIAL CALCULATIONS.

% Gel.	$E_H$	$E_{SO_4}$	$E_B$	$E_x$	$E_z$	$E_z - E_x$	$E_B - 0.02906$	$E'_B$
1	0.01494	0.04563	0.02544	0.00077	0.00878	0.00801	0.00804	0.0371
2	0.02941	0.03749	0.01676	0.00085	0.03215	0.03107	0.03124	0.0603
3	0.03181	0.02824	0.00822	0.00132	0.06210	0.06078	0.06094	0.0900
4	.....	.....	.....	0.00196	0.0825	0.08054	0.08054	0.1095

Since the conductivity of a solution is affected by any change in the number and the mobility of its ions, it was thought that conductivity measurements would furnish information as to the nature of the influence of the gelatin. Measurements were made of the conductivity of 0.1 *M* and 0.01 *M* sulfuric acid solutions which contained different concentrations of gelatin. The concentration of gelatin was varied from 0 to 20%. As it was necessary to apply a correction for the conductivity of the gelatin in conductivity water, a series of measurements was made with gelatin solutions over this same range of concentration. The corrected conductivity values are recorded in Table VI.

TABLE VI.—CONDUCTIVITY OF SULFURIC ACID SOLUTIONS IN PRESENCE OF GELATIN.

% Gel.	0.1 <i>M</i> .	0.01 <i>M</i> .
0	0.037704	0.005011
1	0.033695	0.002413
2	0.030608	0.000948
3	0.027516	0.000755
4	0.02423	0.000686
10	0.009907	0.000462
15	0.003987	0.000349
20	0.002800	0.000233

The effect of the gelatin on the conductivity of the 0.1 *M* and 0.01 *M* sulfuric acid solutions is also shown by the curves in Figs. 4 and 5. The conductivities are plotted as ordinates and the concentrations of gelatin as abscissas. These curves show that the gelatin produces a greater relative change in the conductivity of the 0.01 *M* sulfuric acid solution than in the conductivity of the 0.1 *M* solution. It should be recalled that in the concentration-cell measurements, recorded in Table IV, the gelatin produced a much greater relative change in the hydrogen-ion concentration of the 0.01 *M* solution than in the 0.1 *M*. In fact, by the addition of about 3 to 4% of gelatin, the concentration of the 0.01 *M* solution was reduced practically to zero. From Fig. 5 it is readily seen that by the addition of about 3% of gelatin the conductivity has been reduced almost to zero. This indicates that not only is the hydrogen-ion concentration reduced by the addition of gelatin but that sulfuric acid is removed as a whole.

Several calculations were made involving the conductivity data and potential data in an effort to determine whether the gelatin produced an actual change in the mobility of the ions, but it was impossible to conclude from these calculations whether the effects obtained were due to concentration changes alone or to concentration changes together with changes in mobility or the presence of new ions.

Two explanations have been offered to account for the action of gelatin, one of which assumes that the ions of the acid are "absorbed" by the gelatin, and the other that a highly dissociable chemical compound is formed.



Supporters of the first theory are H. G. Bennett<sup>4</sup> and A. Mutscheller;<sup>2</sup> and favoring the second theory are H. R. Procter,<sup>5</sup> H. R. Procter and J. A. Wilson,<sup>6</sup> J. Loeb,<sup>7</sup> and W. O. Fenn.<sup>8</sup>

It has been shown in this investigation that some of the properties of sulfuric acid are altered by the presence of gelatin. A summary of the data obtained in the work on its influence on the transference number of the anion of sulfuric acid is contained in Table III. It may be observed that the boundary potential ( $E_B$ ) is reduced from  $+0.02906$  to  $-0.00006$ . Corresponding to this decrease in boundary potential, there is an increase in the

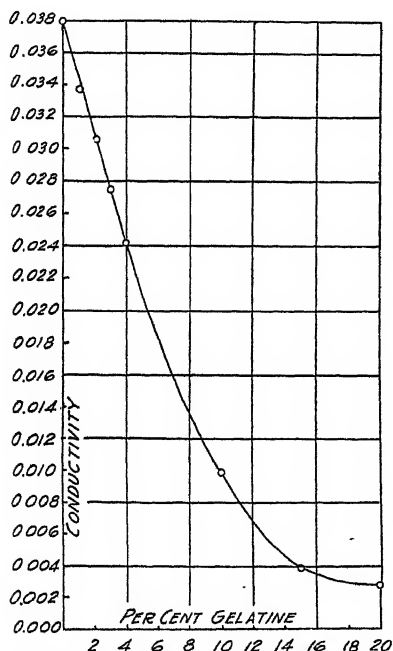


Fig. 4.—Conductivity-gelatin curve for 0.1 M  $H_2SO_4$ .

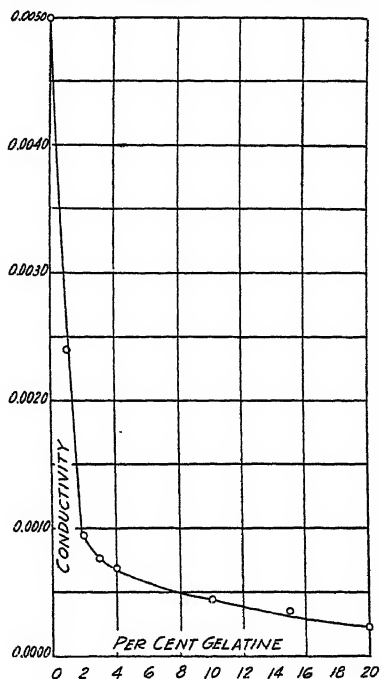


Fig. 5.—Conductivity-gelatin curve for 0.01 M  $H_2SO_4$ .

potential of the hydrogen concentration cell ( $E_H$ ) from 0.01136 to 0.04155 and a decrease in the potential of the sulfate concentration cell ( $E_{SO_4}$ ) from 0.04918 to 0.02068. There is an apparent increase in the transference number of the anion from 0.187 to 0.685. Any factor which would increase the numerical value of  $E_H$  and decrease  $E_{SO_4}$  would give the observed effect of a decrease in the boundary potential and an in-

<sup>4</sup> Bennett, *J. Am. Leather Chem. Assoc.*, 13, 270 (1918).

<sup>5</sup> Procter, *J. Chem. Soc.*, 100, 342-3 (1911); 105, 313 (1914).

<sup>6</sup> Procter and Wilson, *ibid.*, 109, 307 (1916).

<sup>7</sup> Loeb, *J. Gen. Physiol.*, 1, 39-60, 237-54 (1918); 2, 363-85, 483-504, 559-80 (1919).

<sup>8</sup> Fenn, *J. Biol. Chem.*, 33, 279-94, 439-51 (1918); 34, 141-60, 415-28 (1918).

crease in the transference number of the anion. This factor was at first believed to be the result of changes in concentration which are recorded in Table IV, due to the presence of the gelatin. A careful consideration of the boundary potentials  $E_x$ ,  $E_B$ , and  $E_z$  which result from these changes in concentration leads to the conclusion that they should neutralize each other. The data in Table VI show this to be the fact. Therefore this effect was not due to the concentration changes brought about by the introduction of the gelatin. This led to the conclusion that the observed changes in the potentials of the concentration cells resulted from a change in the boundary potentials. This decrease in the boundary potential could be produced by any one of three factors. An actual change in the transference numbers; a decrease in the concentration of the 0.1 *M* solution such that it was less than the 0.01 *M* solution; or by a change in the kind of ions present. Since the second of these factors is eliminated by the data recorded in Table IV, which shows that such concentration changes are impossible, it appears that the decrease in boundary potential must be due only to the other factors.

As there is a possibility that a chemical compound which ionizes is formed, the facts are considered also from this point of view. If such is the case there should be a fairly close relation between the amount of gelatin added and the amount of acid removed. This would explain the decrease in hydrogen-ion concentration and decrease in conductivity observed. If such a reaction occurs new compounds are formed and some of the hydrogen ions are replaced by complex gelatin ions which results in the increase in the transference number of the anion as observed. No data were obtained from which the exact amount of sulfuric acid removed by a definite weight of gelatin could be determined.

From the curve for the conductivity of the 0.1 *M* sulfuric acid solution, Fig. 4, it appears that the conductivity of the solution is reduced a definite amount for each additional per cent. of gelatin. The addition of the first per cent. of gelatin in the 0.01 *M* solution also produces about the same reduction in conductivity. This indicates that a definite quantity of gelatin removes a definite amount of sulfuric acid from the solutions. If the compound formed dissociates, and some evidence has been obtained from other sources that it does, then the conductivity curves will tend to flatten at the higher concentrations of gelatin. Loeb<sup>7</sup> has been led to believe that in acid solutions gelatin reacts to form gelatin salts of the acid and in the case of sulfuric acid he states that the gelatin sulfate formed has the composition represented by the formula  $\text{gel}_4(\text{SO}_4)_2$ . The dissociation of such a salt would result in the formation of a slowly moving complex colloidal gelatin cation and a sulfate anion. The transference number of the anion of such a compound would be greater than that of the cation. This conforms to the observed facts. Furthermore, such a compound

would show some conductivity, so that for the higher concentrations of gelatin the decrease in conductivity would no longer be proportional to the gelatin added. This is borne out by the flattening of the conductivity curves at the higher concentrations of gelatin. It should be pointed out that the sharp bend in the conductivity curve of the 0.01 *M* solution, Fig. 5, occurs at about the same concentration as a similar bend in the gelatin transference-number curve, Fig. 2; furthermore it is shown from the gelatin concentration cells, Table IV, that the sulfuric acid in 0.01 *M* solution is practically all removed at this same concentration of gelatin.

These facts indicate that sulfuric acid as such is removed by the addition of gelatin to the solution. Accordingly the apparent change in transference numbers is due not to an actual change in the velocity of the  $H^+$  and  $SO_4^{--}$  ions, but to the presence of new ions in the solution resulting from the dissociation of the gelatin—sulfate compound.

It is the opinion of the authors that the action of gelatin and sulfuric acid results in the formation of a single dissociable product in which the  $H^+$  ion of the acid loses its identity. It is further believed that in the presence of a base a similar product would result in which the identity of the  $OH^-$  ion would be lost and that in the presence of a neutral salt solution no similar action would result. At the present time investigations are being conducted by the authors to confirm this hypothesis.

### Summary.

1. The effective concentration of 0.1 *M* and 0.01 *M* sulfuric acid solutions has been found to be reduced by the addition of gelatin.
2. The transference numbers of 0.1 *M* and 0.01 *M* sulfuric acid solutions have been found to be altered by the presence of gelatin.
3. The conductivities of sulfuric acid solutions have been found to be reduced by the presence of gelatin.
4. An hypothesis has been offered to account for the action of gelatin in the presence of electrolytes

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## SOLUBILITY VII. SOLUBILITY RELATIONS OF RHOMBIC SULFUR.

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Received June 28, 1921.

The solubility relations of sulfur are of considerable interest in the light of the theory of solubility set forth in the previous papers of this series<sup>1</sup> because liquid sulfur,  $S_\lambda$ , has a rather high internal pressure compared with most liquids and the solubilities of rhombic sulfur should therefore serve well to illustrate the decreasing solubility to be expected as the internal pressure of the solvent decreases.

The solubilities of sulfur have been the subject of frequent investigation. We have data by Étard<sup>2</sup> for hexane, benzene, ethylene bromide and carbon bisulfide; by Gerardin<sup>3</sup> for stannic chloride in the neighborhood of the melting point of sulfur; by Aten<sup>4</sup> for sulfur monochloride; by Smith and Carson<sup>5</sup> for iodine; by Cossa<sup>6</sup> for chloroform, ethyl ether, benzene, carbon disulfide and toluene; by Retgers<sup>7</sup> for methylene iodide; by Brönsted<sup>8</sup> for benzene, iodobenzene and chloroform; by Hoffman<sup>9</sup> for carbon tetrachloride, dichloro-ethylene, ethylene chloride, pentachloro-ethane, perchloro-ethylene, trichloro-ethylene and tetrachloro-ethane. There are other data for more or less polar solvents, including phenol,<sup>10</sup> naphthol<sup>10</sup> and alcohols<sup>11,3</sup> but the only polar solvent we shall consider is ammonia, for which we have data by Ruff and Hecht.<sup>12</sup>

Some of the data referred to are obviously not very accurate, and many of the determinations were made only at one temperature. Accordingly it has been desirable to check certain portions and to supplement others. We have measured solubilities in carbon tetrachloride, benzene, toluene, *m*-xylene, heptane and ethylene chloride.

The sulfur was purified by sublimation. The ethylene chloride was purified by distillation. The carbon tetrachloride, heptane and benzene used were from the stocks

<sup>1</sup> Hildebrand, *THIS JOURNAL*, 38, 1452 (1916); 39, 2297 (1917); 41, 1067 (1919); Hildebrand and Jenks, *ibid.*, 42, 2180 (1920); Hildebrand and Beuhrer, *ibid.*, 42, 2213 (1920). Hildebrand, *ibid.*, 43, 500 (1921).

<sup>2</sup> Étard, *Ann. chim. phys.*, [7] 2, 571 (1894).

<sup>3</sup> Gerardin, *ibid.*, [4] 5, 129 (1865).

<sup>4</sup> Aten, *Z. physik. Chem.*, 54, 86, 124 (1905).

<sup>5</sup> Smith and Carson, *ibid.*, 61, 200 (1909).

<sup>6</sup> Cossa, *Ber.*, 1, 38 (1868).

<sup>7</sup> Retgers, *Z. anorg. Chem.*, 3, 347 (1893).

<sup>8</sup> Brönsted, *Z. physik. Chem.*, 55, 371 (1906).

<sup>9</sup> Hoffman, *Ber.*, 43, 188 (1910).

<sup>10</sup> Smith, Holmes and Hall, *THIS JOURNAL*, 27, 805 (1905).

<sup>11</sup> de Bruyn, *Z. physik. Chem.*, 10, 781 (1892).

<sup>12</sup> Ruff and Hecht, *Z. anorg. Chem.*, 70, 61 (1911).

purified for the recent investigation by us of the solubilities of iodine. The toluene was purified by the method used by Richards and Coombs.<sup>13</sup> The *m*-xylene was purified by a modification of the method described by Levinstein.<sup>14</sup> The *o*- and *p*-xylenes occurring in ordinary xylene were oxidized by treatment with 40% nitric acid until about a third of the original xylene had been destroyed. The *o*- and *p*-toluic acids are formed more readily than the *meta* variety. The xylene remaining was washed with sodium hydroxide and water to remove the acids. Nitro bodies were also formed in this process, which were removed by long reduction, first by hydrochloric acid and tin, then by sodium hydroxide and zinc dust. The liquid was then treated with conc. hydrochloric acid and distilled with steam. The distillate was fractionated thrice, giving a constant fraction boiling at 139.0°.

TABLE I.

## SOLUBILITIES OF SULFUR.

Solvent.	0°.		25°.		35°.		45°.		54°.	
	%.	mol %.	%.	mol %.	%.	mol %.	%.	mol %.	%.	mol %.
Carbon	0.340	0.204	0.827	0.498	1.156	0.697	1.567	0.946	2.010	1.212
tetrachlo-	0.337	0.202	0.834	0.502	1.153	0.695	1.561	0.942	2.005	1.211
ride	...	...	0.832	0.501	1.157	0.698	...	...	...	...
Av.	0.339	0.203	0.831	0.500	1.155	0.697	1.564	0.944	2.008	1.212
Heptane	0.124	0.048	0.362	0.141	0.510	0.200	0.698	0.274	0.925	0.363
	0.123	0.048	0.362	0.141	0.514	0.201	0.698	0.274	0.925	0.363
	...	...	...	...	...	...	0.697	0.273	0.928	0.364
Av.	0.124	0.048	0.362	0.141	0.512	0.201	0.698	0.274	0.926	0.363
Toluene	0.901	0.326	2.015	0.734	2.725	0.996	3.620	1.330	4.86	1.800
	0.892	0.322	2.000	0.727	2.720	0.994	3.620	1.330	4.85	1.796
	...	...	2.040	0.743	2.720	0.994	...	...	4.83	1.791
	...	...	...	...	...	...	...	...	4.86	1.800
Av.	0.897	0.324	2.018	0.735	2.722	0.995	3.620	1.330	4.85	1.797
<i>m</i> -Xylene	...	...	1.970	0.825	...	...	3.610	1.525	...	...
	...	...	1.970	0.825	...	...	3.605	1.524	...	...
	...	...	1.978	0.828	...	...	3.590	1.518	...	...
	...	...	1.965	0.823	...	...	3.610	1.525	...	...
	...	...	1.963	0.822	...	...	...	...	...	...
Av.	...	...	1.969	0.825	...	...	3.604	1.523	...	...
Benzene	...	...	2.072	0.640	...	...	...	...	5.145	1.626
	...	...	2.072	0.640	...	...	...	...	5.170	1.633
	...	...	2.078	0.642	...	...	...	...	5.170	1.633
	...	...	...	...	...	...	...	...	5.180	1.636
	...	...	...	...	...	...	...	...	5.160	1.629
Av.	...	...	2.074	0.641	...	...	...	...	5.165	1.631
							40°	79°		
Ethylene	...	...	0.824	3.195	...	...	1.380	0.537	5.43	2.17
chloride	...	...	0.825	3.202	...	...	1.380	0.537	...	...
	...	...	0.830	3.220	...	...	1.380	0.537	...	...
									97.5°	
	...	...	...	...	...	...	...	...	9.97	4.10
Av.	...	...	0.826	3.206	...	...	1.380	0.537	...	...

<sup>13</sup> Richards and Coombs, *THIS JOURNAL*, **37**, 1668 (1915).<sup>14</sup> Levinstein, *Ber.*, **17**, 444 (1884).

The solubility determinations were made by the aid of the vessel described in the previous investigation, except that the solutions were blown into "ducks" similar to those described in "Physiko-Chemische Messungen," by Ostwald-Luther. In the earlier experiments these "ducks," after weighing, were placed upon an electrically heated plate where the solvent was evaporated. The weight of the sulfur remained constant, upon further heating after the evaporation of the solvent. In the later experiments the solvent was evaporated without heating by blowing a current of air through the vessel. Before weighing, the sulfur was heated to fusion.

Table I contains the results of the determinations from 0° to 54°, expressed in weight percentages, grams of sulfur per 100 g. of solution, and expressed also in mol percentages, mols of sulfur, S<sub>8</sub>, per 100 mols of solution. The figures in the last row for each solvent are the average values. Further observations were made at higher temperatures with benzene, toluene and *m*-xylene, respectively, by making up solutions of known composition and noting the temperature at which a minute residual crystal neither increased or diminished in size when observed through a low-power microscope. These results are given in Table II.

TABLE II.

	Benzene.	Toluene.	<i>m</i> -Xylene.
<i>t</i> .	84°	83.5°	80°
Wt. per cent. ....	13.02	11.64	10.29
Mol. per cent. ....	4.36	4.52	4.53

The results of our own experiments together with most of those of other observers, previously cited,<sup>15</sup> are plotted in Fig. 1, using as ordinate the logarithm of the solubility expressed in terms of mol-fraction, and as abscissa, the reciprocal of the absolute temperature. The significance and value of this method of plotting solubility has been explained in the fifth paper of this series.<sup>16</sup>

### Discussion.

The curves in Fig. 1 show very strikingly the deviations of these solutions from the solubility that would be expected in a solvent with which sulfur obeyed Raoult's law. The line corresponding to the ideal solubility is calculated from the melting point and the heat of fusion of rhombic sulfur, using data given in a paper by Lewis and Randall<sup>17</sup> and corresponds to an ideal solubility for S<sub>8</sub> of mol-fraction 0.282 at 25°. The heat of solution of sulfur in such a solvent is the same as its heat of fusion, or, in other words, such a solvent would mix with molten sulfur with no heat effect.

The position of sulfur in the table of internal pressures given in our third paper may be determined by the aid of the following data. Toepler<sup>18</sup> has given the specific volume of supercooled sulfur at 20° as 0.951 times

<sup>15</sup> The data by Cossa are evidently of inferior accuracy and have been omitted.

<sup>16</sup> See also Braham, *THIS JOURNAL*, 41, 1715 (1919).

<sup>17</sup> Lewis and Randall, *ibid.*, 36, 2468 (1914).

<sup>18</sup> Toepler, *Wied. Ann.*, 47, 169 (1892)

the specific volume at  $120^\circ$ , which according to Pisati<sup>19</sup> is 0.5541. From these figures we calculate the molecular volume of liquid sulfur  $S_8$ , at  $20^\circ$  as 135 cc.

The surface tension of sulfur at  $20^\circ$  is 60.0.<sup>20</sup> This gives  $\gamma/V^{1/3} = 11.7$ , which would place sulfur close to iodine in internal pressure.

From the vapor pressure measurements of Ruff and Graf<sup>21</sup> we calculate the heat of vaporization of sulfur at low temperatures to be 19,100 cal.

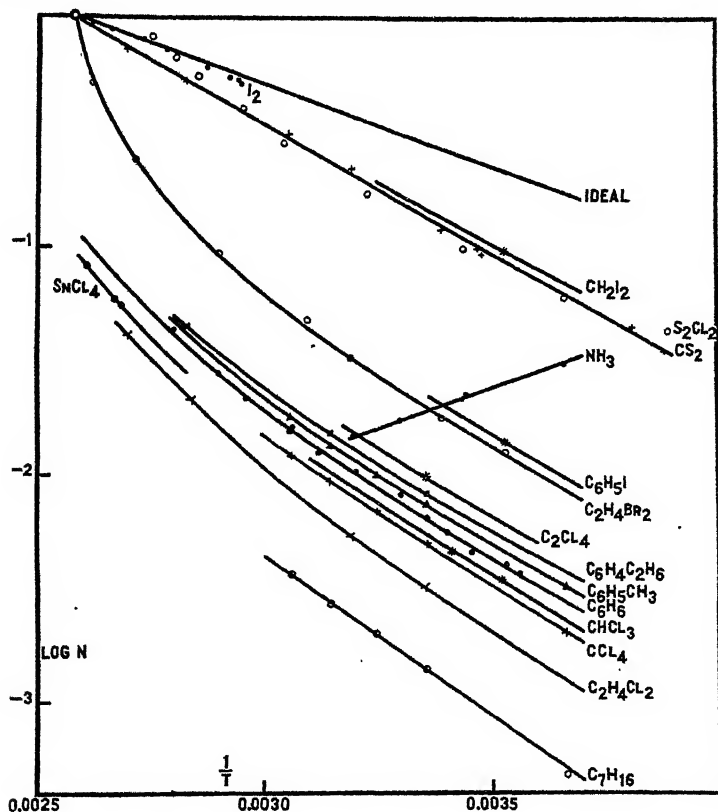


Fig. 1.—Solubilities of rhombic sulfur.

per mol. From this we get  $L_v/V = 137$ , which, again, would place sulfur just above iodine in internal pressure. Unfortunately, data do not exist for the calculation of the internal pressure by the more accurate method of our sixth paper.

We should thus expect that sulfur would obey Raoult's law rather closely with iodine, and that its solubility would decrease progressively as we

<sup>19</sup> Pisati, *Gazz. chim. ital.*, 4, 29 (1874).

<sup>20</sup> Cf. Harkins, Davis and Clark, *THIS JOURNAL*, 39, 541 (1917).

<sup>21</sup> Ruff and Graf, *Ber.*, 40, 4199 (1907).

change to solvents of lower internal pressure. By comparing the curves in the figure with the table of internal pressures given in our third paper the order will be seen to correspond, on the whole, very well.

A minor discrepancy exists in the cases of toluene and xylene. These have internal pressures smaller than that of benzene so that lower solvent power for sulfur would be expected; in the case of xylene about the same as that of carbon tetrachloride. The reason for this discrepancy will be discussed in a future theoretical communication. We will merely note that the expected order is attained at higher temperatures with liquid sulfur. According to observations by Alexejeff<sup>22</sup> the critical temperature of mixing of benzene and sulfur is 163°, whereas with toluene it is 180°. Of course, at these temperatures considerable  $S_\mu$  is present so that they cannot be regarded as true measures of the solubility of  $S\lambda$ .

Ethylene chloride, shows an abnormally low solvent power. Its internal pressure is greater than that of benzene, but its solvent power for sulfur is considerably less than that of carbon tetrachloride. This is undoubtedly due to its polar character, as shown by its dielectric constant of 10.4. The dielectric constant of liquid sulfur is only 3.4. As the polar character diminishes with rising temperature we find the solvent power of ethylene chloride increasing somewhat more rapidly with temperature than does that of a normal substance such as carbon tetrachloride. Ethylene bromide, with a smaller dielectric constant, 4.9, shows a solvent power nearly as great as its internal pressure would lead one to expect. Tetrachloroethylene,  $C_2Cl_4$ , with a dielectric constant of only 2.46 has about the solvent power indicated by its internal pressure. The other solvents investigated by Hoffman have not been included in the plot, partly because of lack of space, partly because of lack of knowledge concerning their physical constants. In general, however, we may state that their solvent powers accord well with the theory.

The figures of Aten for sulfur monochloride show, when plotted, considerable irregularity. Those for hexane by Étard, not included in the plot, are very close to our own for heptane, but a smaller slope than that of the other curves of the family indicates some inaccuracy. The small solubility of sulfur in hexane makes accurate determinations difficult. Étard's figures for benzene also do not fall very closely upon the curve.

Methylene iodide, which was not given in the table of internal pressures, has a value for  $L/V$  of 136, which places it below sulfur monochloride and accords exactly with its solvent power for sulfur.

The curve for ammonia, which is included as an interesting illustration of a solvent power to be attributed to solvation, falls off at higher temperatures, quite unlike the other cases given. The prediction of such

<sup>22</sup> Alexejeff, *Wied. Ann.*, 28, 305 (1886).



behavior is outside the scope of the theory and is part of the great unsolved problem of chemistry, the prediction of chemical combination.

The deviations from Raoult's law for most of the substances here considered is sufficient to cause the existence of two liquid phases above the melting point of sulfur. Therefore, the curves below that of ethylene bromide do not converge to the melting point of sulfur but would be continued to the left as the solubility curves for liquid sulfur, ending at the critical temperatures of mixing. The data for this region are fragmentary and conflicting, so that we have not attempted to include them in this paper.

We may note the possibility offered by such a family of curves of constructing a solubility curve from a single point, as we have done in the figure for methylene iodide, iodobenzene and tetrachloro-ethylene. The solubility of sulfur in these solvents at any desired temperature can be read from such a curve. Such a procedure would not, of course, be valid in the case of a very polar solvent, or of one, like ammonia, which forms a solvate with the sulfur.

In conclusion we would point out the enormous deviations from Raoult's law which most of the solubilities of sulfur represent, the extreme case being with heptane, where the solubility at  $25^{\circ}$  is 0.00141, expressed as mol. fraction, while the solubility according to Raoult's law is 0.282. It is also evident that there is no justification in attempting to account for this variation by the assumption of any abnormal molecular weight for either substance. What is required is a substitute for Raoult's law for defining the ideal solution. The study of this subject is now in progress.

### Summary.

Solubilities of rhombic sulfur at various temperatures have been measured in the following solvents: heptane, ethylene chloride, carbon tetrachloride, benzene, toluene, and *m*-xylene.

These data, together with many obtained by other observers in these and other solvents, have been plotted by the method previously used by us for evaluating solubility data.

It is shown that, with the exception of certain minor discrepancies, the solubilities of sulfur accord well with the internal pressure relations of the substances involved.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SYRACUSE UNIVERSITY.]

## POLYMORPHIC TRANSFORMATIONS OF ANTIMONY TRISULFIDE.

BY SAMUEL WILSON, WITH C. R. MCCROSKY.

Received June 30, 1921.

Between 1878 and 1890 several researches<sup>1,2</sup> on the transformation of the red anhydrous and the orange hydrated forms of antimony trisulfide into the black variety were performed. Those of Ditte<sup>3</sup> and Lang<sup>4</sup> were most significant, but neither investigator worked under rigorously controlled conditions. Lang used aqueous hydrochloric acid at room temperature and found that the time required for transformation of the red form to the black varied inversely with the concentration of the acid employed, ranging from 8 days for a 22% to 150 days for a 1% solution. Ditte worked with the orange-red dihydrate, using excess of acid and high temperatures.

A more quantitative study of this transformation appeared to us desirable. Accordingly the red sulfide was prepared by precipitation with washed hydrogen sulfide from a dil. tartar emetic solution acidified with tartaric acid. The precipitate was washed in succession with water, potassium carbonate solution, water, tartaric acid solution, water, alcohol, carbon disulfide and ether, then dried at 110°. The brick-red amorphous sulfide thus obtained was powdered and passed through a 40-mesh screen,

The first series of experiments was carried on with 2g. samples of the sulfide in small flasks. Five-cc. portions of the reagent were added, the flask stoppered and examined at regular intervals to note whether a change to the black form had occurred. The temperature ranged from 18° to 22°. As reagents hydrochloric acid of 1 *N*, 7 *N*, and 12 *N* concentrations, 7 *N* phosphoric acid; 7 *N* sulfuric acid; glacial and 1 *N* acetic acid, and an ether solution saturated with dry hydrogen chloride were employed. Of these, only the hydrochloric acid solutions in water gave any appreciable transformation, even after the lapse of two months. The time required for these was much less than for those found by Lang. For 12 *N*, 7 *N* and 1 *N* hydrochloric acid, the time required for transformation was 0.5 day, 1 day and 10.5 days, respectively.

Time measurements in all cases were made to the point of final transformation, that is, until no more red particles could be seen. At lower temperatures the transformation is gradual, the finer particles changing first, but it speeds up towards the end, and at higher temperatures is so rapid that the eye can scarcely measure the time interval between incipient and final transformation.

<sup>1</sup> Clermont and Frommel, *Compt. rend.*, 86, 87 (1878).

<sup>2</sup> Scheuerman, *Ann.*, 249, 339 (1888).

<sup>3</sup> Ditte, *Compt. rend.*, 102, 212 (1886).

<sup>4</sup> Lang, *Ber.*, 18, 2716 (1885).

The difference between the above results and those of Lang may be due in part to the greater fineness of our particles, but it is more probably explained by the fact that Lang permitted the evolved hydrogen sulfide to escape, thus constantly displacing the equilibrium, whereas in these experiments all the flasks were carefully stoppered.

The action is due, apparently, to a solution of the red sulfide in the acid, followed by a reprecipitation of the less soluble black modification. These black crystals under the microscope showed the characteristic orthorhombic faces of the mineral stibnite.

Further experiments were made to determine the effect of temperature on the velocity of transformation. A 20% hydrochloric acid solution was used, with the same proportions of acid and red sulfide as before. The experiments were carried out in a thermostat at a series of temperatures up to 75° with a maximum variation of 0.5°; 25cm. test-tubes were used instead of flasks.

Temperature. °C.	Time required.	
	Hrs.	Min.
26.5	44	..
30	29	..
35	16	..
40	9	..
68.5	..	62
75	..	32

The very rapid increase of speed of transformation with rise of temperature is noteworthy.

Under similar conditions, a 20% solution of hydrobromic acid gave no visible blackening, even after 20 hours at 75°.

SYRACUSE, NEW YORK.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

## THE REDUCTION OF COPPER OXIDE BY HYDROGEN.

BY ROBERT N. PEASE AND HUGH STOTT TAYLOR.

Received July 5, 1921.

This investigation of the reduction of copper oxide by hydrogen was undertaken in the hope that the results might throw some light on the mechanism of the catalytic combination of hydrogen and oxygen in the presence of metallic copper, in a study of which we have been engaged.<sup>1</sup> Since copper oxide may be reduced by hydrogen and the resulting copper may be re-oxidized without difficulty at temperatures at which the metal is catalytically active, it would appear that, in all probability, the catalytic reaction proceeded as a result of the alternate oxidation and reduction of the copper. Certain of our results were apparently inconsistent

<sup>1</sup> The results of this investigation will be published shortly.

with this interpretation, however, and it was thought that a study of the reduction reaction by itself might be of assistance in clearing up the discrepancy. As an examination of the literature revealed that this reaction possessed several peculiarities of its own, the investigation seemed the more worth while.

A rather extensive investigation of the reduction of copper oxide by hydrogen has been carried out by Wright, Luff and Rennie.<sup>2</sup> Hydrogen was passed at a constant rate through a U-tube containing copper oxide held at various fixed temperatures by means of vapor baths and the rate of reduction determined by weighing the U-tube from time to time. It was found that the reduction was preceded by an "incubation" period, the length of which was greater the lower the temperature. Following the incubation period, (during which there was no perceptible reaction) reduction set in at a steadily increasing rate (induction period) till a maximum was reached, after which the rate decreased gradually to zero as the reaction approached completion. Experiments were carried out at several temperatures between 130° and 257°. In other experiments, copper oxide was spread on the bottom of a small flask heated in a vapor bath, and a current of hydrogen was passed through the flask. The authors' description of the progress of the reaction is instructive. "The reduction commenced visibly by the formation of a red speck amongst the little mass of copper oxide at the lowest part of the bulb; this quickly spread, becoming rapidly larger and larger until practically the whole mass became a reddish metallic powder, the progress of the reaction reminding one of the slow deflagration of a quantity of touch paper, *the reducing action being apparently propagated from particle to particle through the mass.*" This occurred, be it remembered, in the presence of an excess of hydrogen.

It is evident from these results that the reaction is auto-catalytic, copper being the auto-catalyst, in all probability. The reaction starts only after some time—at least as evidenced by the change in weight of the tube containing the oxide<sup>3</sup>—with the formation of one or more visible nuclei of copper. From these as centers, the zone of reaction, that is, the copper-copper oxide interface, spreads out and as its area increases the rate of water formation increases.

If the induction period is due to the initial absence of metallic copper, it should be possible to shorten it or cause it to disappear altogether by adding already reduced copper to the oxide about to be reduced. It seemed

<sup>2</sup> Wright, Luff and Rennie, *J. Chem. Soc.*, 33, 1 (1878); 35, 475 (1879).

<sup>3</sup> That the tube does not lose weight during the first part of the run does not necessarily prove that reaction is not taking place at an exceedingly slow though steadily increasing rate. Various sources of error, particularly the retention of the water formed through adsorption, might obliterate any effect of the expected magnitude. The reproducibility of the results would indicate that the reaction does not start merely by accident.

worth while to try to confirm this experimentally. Further, since water as well as copper is a product of the reaction, it was decided to determine the effect of adding more water to the system as moisture in the hydrogen.

### Experimental.

A sketch of our apparatus is shown in Figure 1.

Electrolytic hydrogen from the tank A was passed through heated palladized asbestos in the tube B to convert the small percentage of oxygen present in the hydrogen to water, through the flow-meter C, the phosphorus pentoxide drying-tube D and then through the electrically heated furnace E, which contained the copper oxide. The

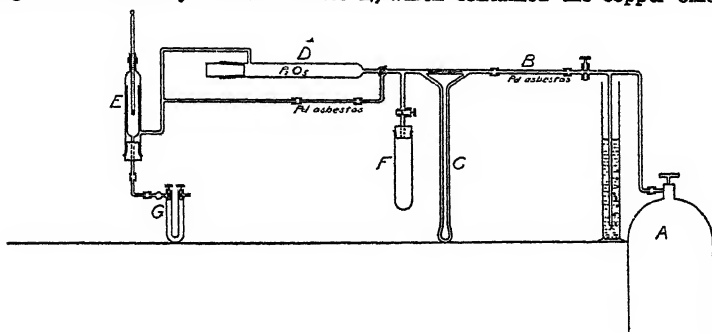


Fig. 1.—Apparatus.

furnace consisted of two concentric glass tubes, the inner one of which contained the oxide. The outer tube was wound with Nichrome wire and was covered with magnesia pipe covering. Rates of reduction were measured by determining the rates of water formation. This was accomplished by passing the effluent hydrogen through a U-tube containing calcium chloride (G) for definite time intervals and noting the increase in weight due to water absorbed. The rate of reduction is expressed throughout in terms of milligrams of water absorbed by the calcium chloride tube in 5 minutes' passage of the effluent hydrogen. The rate of flow of the hydrogen was maintained constant at 50 cc. per minute. Samples of 5 cc. apparent volume of copper oxide, weighing within a few tenths of 10 g. were always employed. As the containing tube was 2.5 sq. cm. in cross section, this gave a layer of copper oxide about 2 cm. deep. An imported copper oxide in granules intended for organic analysis, "hirsekorngrosse," (about 10- to 20-mesh) was used.

For the purpose of checking the results of Wright, Luff and Rennie as to the character of the reaction and in order that we might have standards with which to compare our other experiments, we have obtained reduction curves at 150° and 200°. These are presented in Fig. 2. It will be seen that these possess the characteristics reported by the above authors. There is the incubation period (practically non-existent at 200°) followed by the period of increasing rate of reduction to a maximum and finally the period of decreasing rate. At 200° the maximum rate of reduction corresponded to the formation of 130 mg. of water in 5 minutes. If all the hydrogen had been consumed the rate of formation of water would have been 184 mg. in 5 minutes. Although the design of the furnace

prevented direct visual observations of the progress of the reaction, its characteristics were made clear by an examination of samples in various stages of reduction. It was found that reduction *practically never started at the top*, where the preheated hydrogen first met the charge, but usually at some point near the middle of the charge along the side of the tube. From these points as nuclei, the reaction zone appeared to spread over the whole mass.

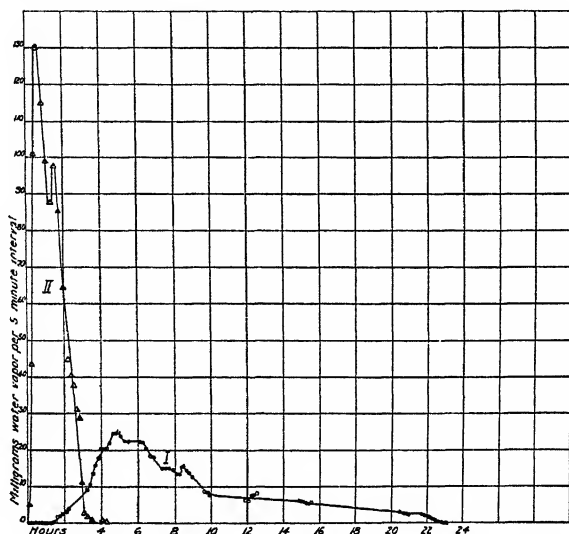


Fig. 2.—Reduction of copper oxide by hydrogen. Curve I, reduction at 150°. Curve II, reduction at 200°.

**Effect of Copper.**—In one experiment, a layer of previously reduced granules was placed on top of the oxide, which was then treated with hydrogen at 150°. The result is shown graphically by Curve II, Fig. 3. Curve I represents the standard reduction with pure copper oxide and hydrogen. It is the initial portion of Curve I, Fig. 2 on a larger scale. By comparing the curves it may be seen that the layer of copper considerably hastened the setting-in of the reaction and nearly eliminated the incubation period. An examination of the sample after reduction had proceeded for several hours showed that the reaction had begun at the top of the charge in contact with the copper and had proceeded downward in wave front roughly normal to the direction of hydrogen flow. Since ordinarily reduction begins within the charge rather than at its surface, the top being reduced toward the end instead of at the beginning of the run, it would appear that the layer of copper had rendered the oxide in contact with it the more reactive, substantiating the assumption that the reaction is autocatalytic and takes place mainly and most easily at a copper-copper

oxide interface. The reaction did not subsequently reach as high a rate as did the standard, as the curve shows. Ordinarily, the reaction starting at some point within the charge, the area of the interface will be at least twice the cross-sectional area of the tube since there will be an interface above and another below the reduced portion. In the case described above the area of the interface was only that of the cross-section of the tube, and, as it is thought that the rate of water formation is proportional to the interface area, the reaction would not be expected to reach as high rates as it did in the standard run, since the interface area is only about half as great.

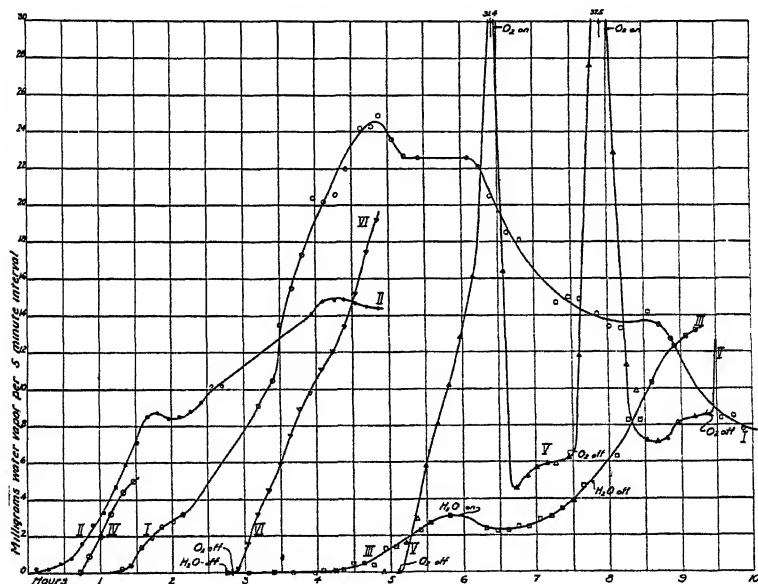


Fig. 3.—Reduction at 150°. Curve I, Normal reduction. Curve II, in presence of metallic copper. Curve III, effect of water vapor; 5 mg. per 5-minute interval. Curve IV, effect of preliminary treatment with dry air. Curve V, effect of oxygen equivalent to 10 mg. of water per 5-minute interval. Curve VI, effect of oxygen equivalent to 5 mg. of water per 5-minute interval.

**Effect of Water Vapor.**—Water vapor was added to the hydrogen in the following manner.—An electrolytic gas generator F (Fig. 1), consisting of a wide mouth test-tube containing caustic soda solution in which were immersed 2 spiral nickel wire electrodes, was connected to the hydrogen line. By connecting the electrodes of the generator in series with a variable resistance and a milliammeter, electrolytic gas could be generated at a definite rate into the hydrogen stream, and, by causing the latter subsequently to pass over heated palladized asbestos, the electrolytic gas could be reconverted into water vapor. In these experiments, the cell was

run at such a rate that 5 mg. of water was decomposed (and subsequently synthesized over the palladized asbestos) in 5 minutes. The milliammeter setting was 0.180 amperes. In the 250 cc. of hydrogen which was passed in 5 minutes, this is equivalent to about 2.7% water vapor by volume. This amounts practically to saturation at room temperature. The result of passing this saturated hydrogen over copper oxide at 150° is shown by Curve III, Fig. 3. Not only was reduction prevented during the exposure (reduction would normally have started in 1 to 1½ hours) but in addition did not start for nearly 2 hours after the electrolytic gas was shut off and pure dry hydrogen alone passed over the oxide.

From these results it is clear that water vapor strongly inhibits the initial reaction between hydrogen and copper oxide—that is, it effectively prevents, at this temperature, the formation of copper nuclei. Since it is a product of the reaction it clearly has no such powerful action on the subsequent reaction at the interface. This was confirmed by adding water vapor to the hydrogen again some time after reaction had started. Referring again to Curve III, Fig. 3, it is seen that under these conditions, after an apparent temporary set-back, the reaction proceeded in much the normal fashion.

That the system experienced an exceptionally long incubation period even after the water vapor was shut off suggested that possibly adsorbed water was partially responsible for this phenomenon in the ordinary runs, especially since water vapor so strongly inhibits the preliminary reaction. Accordingly, the effect was tried of drawing dry air through the charge at 150° for 3 hours prior to reduction in order to sweep out any moisture. Air dried by means of a calcium chloride tower was aspirated through the sample at the rate of 50 cc. per minute. At the end of 3 hours, the sample was cooled nearly to room temperature, the air then displaced by hydrogen and the temperature again raised to 150°. The reduction proceeded according to Curve IV, Fig. 3. The result was that the incubation period was reduced to about half its normal length but was not completely wiped out. It would appear, therefore, that the presence of adsorbed water is not alone responsible for the incubation period.

According to Wright, Luff and Rennie,<sup>2</sup> when air (probably undried) was drawn over heated copper oxide for 15 minutes and then the hydrogen current substituted, the incubation period was considerably lengthened. We believe this to be due to the fact that moist air was used and the air swept out by hydrogen while the oxide was hot, when a small quantity of water would certainly be formed, the water absorbed from the air and that formed by catalytic combination being sufficient to retard the reaction.

At 200°, the effect of water vapor was to cause a definite though brief incubation period when none was normally noted. (Curve II, Fig. 4. Curve I refers to the normal reduction.) It did not prevent the reaction



starting, as it did at  $150^{\circ}$ , however. After having once started, the reaction proceeded normally, as was to be expected if water vapor does not affect the reaction at the copper-copper oxide interface.

**Effect of Oxygen.**—Results obtained during the experiments on the catalytic combination of hydrogen and oxygen in the presence of copper indicated that the oxygen present inhibited the reduction of the oxide formed simultaneously with the water, for when the oxygen was shut off, the rate of water formation always rose temporarily to a value considerably greater than that when oxygen had been present.

Further evidence that oxygen inhibits the reduction of copper oxide by hydrogen is afforded by some experiments of Bone and Wheeler.<sup>4</sup> Using a method involving circulation of the gases in a closed system, one part of which was a heated tube containing copper oxide, they found that the rate of consumption of hydrogen from a mixture of 2 parts of hydrogen and 1 part of nitrogen was nearly 10 times as great as from electrolytic gas (2 parts of hydrogen and 1 part of oxygen). The experiments were carried out at  $214^{\circ}$ . It can hardly be assumed that the nitrogen accelerated the reaction; rather would it appear that, with electrolytic gas, the oxygen present inhibits the reduction to such an extent that the combined

rates of reduction and hydrogen-oxygen combination are less than the normal rate of reduction in the absence of oxygen.

For the purpose of confirming these indications, the rates of reduction of copper by hydrogen containing oxygen were determined. Oxygen was added to the hydrogen by connecting with the hydrogen line the electrolytic gas generator used in the experiments with water vapor. The oxygen concentrations are expressed in terms of the corresponding weight

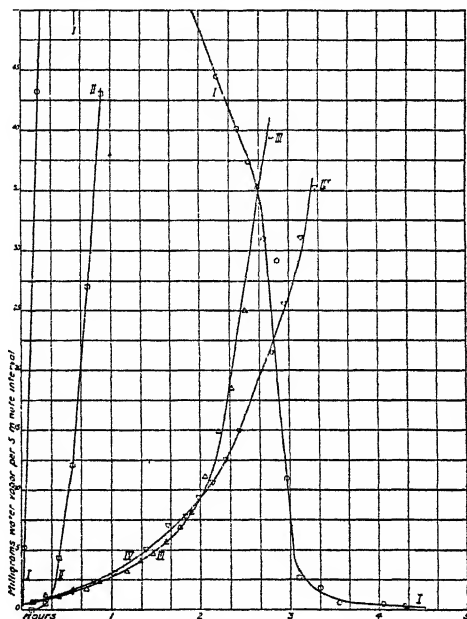


Fig. 4.—Reduction at  $200^{\circ}$ . Curve I, normal reduction. Curve II, effect of water vapor: 5 mg. per 5-minute interval. Curve III, effect of oxygen equivalent to 5 mg. per 5-minute interval. Curve IV, effect of oxygen equivalent to 10 mg. per 5-minute interval.

<sup>4</sup> Bone and Wheeler, *Phil. Trans.*, 206A, 1 (1906).

of water in milligrams which could theoretically be formed from the oxygen during a 5-minute passage of the mixture. Thus, "oxygen equivalent to 10 mg. of water per 5-minute interval" means that the quantity of oxygen present in the hydrogen passed through the apparatus in 5 minutes was sufficient to form 10 mg. of water. This is equivalent to 2.5% of oxygen by volume at 25°, the hydrogen being run at the rate of 50 cc. per minute.

As had been anticipated, it was found that the presence of oxygen very seriously interfered with the reduction reaction. In one experiment, hydrogen containing oxygen equivalent to 10 mg. of water per 5-minute interval was passed over copper oxide for 5 hours, during which period no formation of water could be detected. It appears, therefore, that under these conditions the oxide is not appreciably reduced nor does it possess appreciable catalytic activity toward the combination of hydrogen and oxygen. (Curve V, Fig. 3.) Normally, with pure hydrogen, reduction would have become measurable in 1 to 1½ hours. Directly the oxygen was cut off, reduction set in, the maximum rate being much greater than in any other runs. The incubation period was therefore eliminated by this treatment. It will be recalled that similar treatment with water vapor only resulted in postponing the incubation period. After reduction had been allowed to proceed for a short time, oxygen was again turned on. As a result, the rate of reduction was very markedly repressed, dropping from 31 to 5 mg. of water per 5-minute interval, and did not recover until the oxygen was shut off. Subsequent addition of oxygen resulted in a repetition of this effect.

As Curve VI, Fig. 3, shows, oxygen equivalent to 5 mg. of water per 5-minute interval produces similar effects.

At 200°, (Curves III and IV, Fig. 4), the effect of oxygen was to retard the reduction very strongly though the latter was not completely prevented. The quantities of water formed under these conditions are undoubtedly due in part to catalytic combination; nevertheless, it is clear from the curve that at the end of 3 hours, the charge had not been appreciably reduced whereas reduction would normally have been nearly complete at the end of this time.

The effects produced by oxygen are seen to be quite distinct from those produced by water vapor. (It was possible that they might have been due to the formation of the latter.) At 150°, preliminary treatment with hydrogen containing water vapor not only results in no water formation but postpones the incubation period till the water vapor is cut off. After reduction has commenced, however, further addition of water vapor has no marked effect. With oxygen in the hydrogen, on the other hand, the incubation period is eliminated (that is to say, reaction starts directly the oxygen is cut off) although no reduction takes place during the exposure; but addition of oxygen after reduction has started very markedly represses

the reaction. Clearly water vapor is only effective in the initial reaction between hydrogen and copper oxide. This may be attributed to the strong adsorption of water vapor by copper oxide. Comparisons of the quantities of water added to the hydrogen and quantities recovered from the effluent hydrogen during the first few minutes of the exposures to water vapor indicated that quite large quantities of water vapor must have been taken up. Oxygen, on the other hand, probably is effective only in the reaction taking place at the interface. At first sight it would appear that it also inhibits the initial reaction. However, the fact that reduction commenced directly the oxygen was cut off seems to indicate that the formation of copper nuclei had been going on during this period; that is to say, the elimination of the incubation period is taken to indicate that the primary reaction had taken place even in the presence of oxygen. The abnormally rapid rise to an abnormally high maximum after the oxygen had been turned off and reduction once started further indicates the existence at that time of numerous centers of activity. This is consistent with the observations of Dr. A. F. Benton in this laboratory that oxygen is not markedly adsorbed by copper oxide, at these temperatures.

It has been suggested that the retarding effect of oxygen on the reaction at the interface is due to its adsorption by the interface. It is a little difficult to conceive of oxygen remaining long in the adsorbed state at the interface, the seat of activity in the reduction reaction. Granting that oxygen may be so adsorbed, it would seem very probable that it would either immediately be converted to oxide or else react directly with hydrogen to form water (and such a view of the catalytic reaction has its advantages). The reaction to form oxide, if carried far enough, would eventually decrease the area of the interface materially and hence the rate of water formation. Thus, qualitatively, the effect of oxygen would be accounted for. However, the effect of the oxygen is immediate and it is doubtful whether sufficient oxygen is initially present to reduce the interface area by the required amount. This would certainly require all the oxygen present in the gas for a considerable time and yet it is known that even starting with a pure copper surface, the major part of the oxygen goes to form water, although the remainder does combine to form oxide. It is perhaps more satisfactory to assume for the present that oxygen is in fact strongly adsorbed by the interface and protects it from the hydrogen, and although constantly being consumed in the formation of water and oxide, is nevertheless renewed at a sufficiently rapid rate to maintain the protective film.

### Summary.

1. An investigation of the characteristics of the reduction of copper oxide by hydrogen and the effect on the reaction of adding metallic copper

to the oxide and water vapor and oxygen to the hydrogen has been carried out.

2. It has been pointed out that the reaction is auto-catalytic, copper being the auto-catalyst. The reaction thus appears to take place at the copper-copper oxide interface. This is shown by the character of the reduction curve and the fact that addition of metallic copper accelerates the reaction.

3. It has been shown that the presence of water vapor in the hydrogen markedly interferes with the formation of the original copper nuclei from which the reaction zone, that is, the copper-copper oxide interface spreads out; it does not markedly affect the subsequent reaction at the interface, however.

4. The presence of oxygen in the hydrogen strongly inhibits the reaction at the interface but in all probability has no marked effect on the primary reaction, that is, the formation of the original copper nuclei.

PRINCETON, NEW JERSEY.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY.]

## THE HEATS OF SOLUTION AND OF TRANSFORMATION OF THE ACIDO AND AQUO COBALT PENTAMMINES.

BY ARTHUR B. LAMB AND JOHN P. SIMMONS.\*

Received July 11, 1921.

### Introduction.

The spontaneous transformations of a number of the acido cobalt pentammines into their corresponding aquo compounds have been carefully studied.<sup>1</sup> They have been found to go nearly to completion at ordinary temperatures in aqueous solutions and, as regards velocity, to follow the course of a monomolecular reaction. At higher temperatures the reaction becomes more evidently reversible, and it has been shown that an equilibrium is attained which strikingly resembles the dissociation equilibria of strong electrolytes in water.

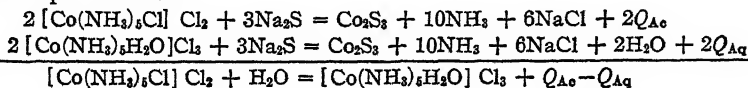
Particularly because of this wider bearing of the subject we have investigated the heat changes accompanying a number of these transformations in aqueous solution. These heat changes could be calculated from equilibria data at different temperatures, did such exist, but unfortunately there are experimental difficulties in studying these equilibria except within a narrow temperature interval. We have therefore been

\* This paper is largely based on a dissertation of the same title submitted by J. P. Simmons in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, 1912.

<sup>1</sup> Lamb and Marden, *THIS JOURNAL*, 33, 1873 (1911).

obliged to employ a direct method of measurement; direct, at least in the sense that only thermal quantities are measured. A really direct measurement of the heat of reaction would be difficult, not only because the most rapid of these transformations are relatively slow, but also because the ammines are for the most part far too insoluble to furnish solutions of adequate concentration.

The method which we have employed depends upon the use of an aqueous solution of sodium sulfide, which reacts rapidly at room temperatures with both the acido and aquo ammines, and produces the same substances in identical amount, except for the liberation of a molecule of water from the aquo ammine.



The difference then in its heat of reaction with an acido ammine on the one hand and with the corresponding aquo ammine on the other will evidently be equal to the heat of transformation of the acido into the aquo ammine.

The rigor of this method evidently depends on the precise identity of the products formed from the acido and the corresponding aquo ammine. The sulfide of cobalt is the only one of the products affording any possibility of dissimilarity. There was no indication whatever that such a dissimilarity existed, and yet the matter was of such fundamental importance that a careful study of the composition of the sulfide formed from the chloro- and the aquo-pentammine chlorides was made. The two sulfides were prepared under the same conditions as prevailed during an actual calorimetric determination, and were then carefully analyzed for sulfur. The chloro-pentammine for these experiments was an imported preparation which had been proved pure by repeated analyses.

The aquo-pentammine chloride was prepared and purified by Jørgensen's method.<sup>2</sup> The ionizable chlorine in the chloro-pentammine was determined by precipitating with silver nitrate solution at 0°, and rapidly coagulating and filtering off the silver chloride. Two samples weighing about 0.4 g. gave 28.27 and 28.24% of chlorine, while the theoretical percentage is 28.31. The aquo-pentammine chloride was analyzed for total chlorine by warming gently with an excess of silver nitrate solution. Two 0.5g. samples gave 39.56 and 39.52% of chlorine, while the theoretical composition is 39.62% of chlorine. These analyses establish the purity of these salts.

The compositions of the cobalt sulfide precipitates were determined by starting from weighed quantities of the ammines, precipitating with sodium sulfide, washing the precipitate from sodium chloride, ammonia, and the excess of the precipitant, and oxidizing the sulfide to sulfate by an ammoniacal solution of hydrogen peroxide, acidifying, and precipitating the sulfate as barium sulfate. The chief difficulty in this analysis lies in the sensitiveness of the cobalt sulfide to oxidation to sulfate by the oxygen of the air during the process of precipitation and washing. This difficulty was successfully overcome by precipitating, washing, and filtering the sulfide in an atmosphere of hydrogen.

<sup>2</sup> Jørgensen, *Z. anorg. Chem.*, 17, 455 (1898).

The apparatus for this purpose consisted of a Gooch adapter set in a suction flask by means of a tight-fitting rubber stopper. In the top of the adapter was a 3-hole rubber stopper containing a connection to a Kipp generator for hydrogen, a dropping funnel with a stopcock, and an outlet of glass tubing with a stopcock attached. By proper manipulation of the stopcocks air was expelled by hydrogen; sodium sulfide and wash water were admitted, and filtration accelerated. At the bottom of the adapter was an asbestos filter between two perforated porcelain disks.

Weighed samples of the ammines were placed upon the filter and hydrogen gas run through the apparatus for several hours. Fifty cc. of sodium sulfide solution was then introduced and the closed apparatus shaken to bring about complete reaction with the ammine. After standing for some time the solution was filtered off, freshly boiled water introduced, and the shaking and filtration were repeated. The process as a whole was then repeated several times until the wash-water no longer gave a test for sodium.

The precipitate was converted to a cobaltic ammine sulfate by standing for 48 hours in an ammoniacal solution of hydrogen peroxide. To recover any sulfate which might have entered into complex combination with the cobalt, the ammine was decomposed by boiling with sodium hydroxide until no more fumes of ammonia were given off. The resulting cobaltic hydroxide was then dissolved in an excess of hydrochloric acid, heated to boiling, and a hot solution of barium chloride added with constant stirring. The barium sulfate was filtered off after 24 hours. By this method the sulfide from the acido ammine gave 45.29% and 45.11% (mean 45.19%) of sulfur; that from the aquo ammine 45.10% and 45.06% (mean, 45.08%) of sulfur. The calculated percentages of sulfur in  $\text{CoS}$ ,  $\text{Co}_2\text{S}_3$ , and  $\text{CoS}_2$  are 35.16, 44.86 and 52.03 respectively. The results are evidently in very close agreement with the requirements of the formula  $\text{Co}_2\text{S}_3$ . The slight excess of sulfur which they indicate is scarcely more than the experimental inaccuracy, and is in the direction that would be anticipated, since any incompleteness either in the washing of the cobaltic sulfide or of the barium sulfate would tend to give too high values for the sulfur. Furthermore, the values for the sulfides from the acido and aquo salts are in still closer agreement, so that there can be no question but what the same sulfide is formed in each case.

Preliminary experiments showed that the heats of reaction with the sodium sulfide solution were very small; indeed so small that even with the saturated solution of the ammines the temperature change would amount to only a few thousandths of a degree. We were obliged therefore to work with a suspension of the solid ammines, although this complicated the measurements by the introduction of the unknown heats of solution. To obviate this difficulty we have made independent determinations of the heats of solution of the ammines concerned.

### Apparatus and Method.

Both the apparatus and the method employed in measuring the heats of solution and of transformation were very simple. The apparatus consisted of a 1-liter Dewar flask, almost completely submerged in a water thermostat and provided with a stopper

into which a Beckmann thermometer, a container for the powdered ammine and a rotary stirrer were fitted. The container consisted of a narrow glass tube extending through a hole in the rubber stopper with an enlarged cylindrical lower portion whose volume was about 10 cc. This enlarged portion was open at the bottom, but its lower rim was ground flat so that a thin microscope cover-glass could be tightly cemented to it. A glass rod extended through the narrow tube from above the stopper and worked tightly in a rubber packing placed at the entrance to the enlarged portion. By pushing this rod downward, the cover-glass could be broken and the cobalt ammine in the container projected into the surrounding water, or sodium sulfide solution. The method of procedure was simply to stir the measured volume of liquid in the Dewar flask until a constant rate of change was shown by the Beckmann thermometer; the weighed quantity of ammine in the container was then discharged into the liquid and the stirring and thermometer readings continued until a constant rate of temperature change had again been established. These readings were plotted, and by an inspection of the curves the temperature change produced by the solution or decomposition of the cobalt ammine could be ascertained.

Preliminary experiments showed that these temperature changes, particularly those produced by the decompositions, were still very small, even when several grams of the cobalt amines was used. This could have been partially remedied by decreasing the quantity of water, or of sodium sulfide solution, and by using a smaller Dewar flask, but this would have increased the relative uncertainty in the heat capacity of the Dewar flask. The only alternative was to reduce the experimental errors as far as possible.

The uniformity in bore and the value of a degree of the Beckmann thermometer were first investigated. Fortunately, over the range used in these experiments, the bore was quite regular, no correction greater than  $0.002^\circ$  having to be applied. By comparison at two different temperatures with a standard thermometer reading to  $0.001^\circ$ , which in turn had been compared with the primary standards at the Bureau of Standards in Washington, one degree of the Beckmann scale was found to be equivalent to  $1.014^\circ$  at  $25^\circ$  on the hydrogen scale. This correction has been applied in all the following measurements.

With such small heat changes to be measured the frictional heat produced by the stirring might evidently amount to a considerable fraction of the total heat change. This would not necessarily involve any error, for, by continuing the stirring after the reaction had ended, as outlined above, a correction could be applied to each experiment which would include both this effect and any heat change due to radiation or conduction. An error from this cause would creep in only if the rate of stirring were not sufficiently constant to prevent any perceptible variation in the rate at which the frictional heat was supplied. Experiments were therefore undertaken to determine the magnitude of the frictional heating effect and its variation with the rate of stirring.

In these experiments, the temperatures of the liquid in the flask and of the air in the room were brought to nearly the temperature of the thermostat ( $25^\circ$ ) and kept at that temperature for some time with intermittent stirring to allow a complete equalization of the temperature throughout the flask, stirrer, container and thermometer. The small stirrer was then rotated at a constant speed and readings of the Beckmann thermometer were taken at regular intervals. The speed was determined by counting the number of revolutions per minute of the belt driving the stirrer, one revolution of the belt being equivalent to about 10 revolutions of the stirrer. With 900 cc. of a sodium sulfide solution in the Dewar flask, very small heating effects were produced, but when this solution was replaced by a similar one of the same strength which had reacted with 8 g. of acido-pentammine chloride, much larger heating effects were obtained. This, however, is not surprising in view of the fine state of subdivision of the precipitate and its rather flocculent nature, for these factors doubtless increase the viscosity very consider-

ably. Indeed it is possible that the increased heating effect might be used as a means of measuring viscosity. With speeds of 50 and 104 revolutions of the belt per minute heating effects of  $0.0015^{\circ}$  and  $0.0060^{\circ}$  per minute, respectively, were obtained. Taking readings every two minutes and stirring but 10 seconds before each reading, heating effects of but  $0.0003^{\circ}$  and  $0.0008^{\circ}$ , respectively, per minute were found. As 10 seconds' intermittent stirring at the lower rate proved sufficient to give uniform temperature readings on the thermometer, this mode of stirring was adopted in all the following measurements. Although the frictional heat was evidently greatly reduced by this procedure its total effect over the 30 minute interval of an experiment was still relatively large and the effect of variation in speed of stirring upon it therefore required consideration. To determine this effect, the rates of heating in the above experiments and in other similar experiments with sodium sulfide suspensions with continuous stirring, were plotted against the rates of stirring. Nearly linear curves were obtained over the short intervals used, whose slope corresponded to an acceleration in the rate of heating of  $0.00003^{\circ}$  per minute for an acceleration in the rate of stirring of one revolution of the belt per minute; or, at a speed of 55 revolutions per minute, to about a 1% increase in the heating effect. Since a constant rate was always attained in the following experiments within 30 minutes after the introduction of the ammine, and the heating effect in the cobalt sulfide suspensions with intermittent stirring was  $0.0003^{\circ}$  per minute, an uncertainty of 10 revolutions per minute in the rate of stirring would result in an uncertainty in temperature over this interval of less than  $0.001^{\circ}$ . This constancy was easily attained even with intermittent stirring.

Similar experiments were made to test the effect of variations in the temperature of the surroundings on the temperature of the liquid in the Dewar flask. With liquid, thermostat, and air, all at very nearly  $25^{\circ}$  a constant rate of stirring was maintained for some time and regular readings of the thermometer were taken. A constant temperature change of  $0.0010^{\circ}$  per minute was obtained under these conditions. After this constant rate had been maintained for some time the temperature of the liquid in the flask was raised  $1^{\circ}$  and another series of readings made. The temperature rise was found to be  $0.0009^{\circ}$  per minute. Finally, the original temperature was re-established in the flask but the temperature of the surrounding air was lowered  $5^{\circ}$ . The consequence was a lesser rate of temperature increase, namely  $0.0003^{\circ}$  per minute. These results show that a temperature difference of  $1^{\circ}$  between the liquid in the flask and the thermostat produces a cooling effect of  $0.0001^{\circ}$  per minute, while a similar difference in temperature between the liquid in the flask and the air produces a cooling effect of  $0.00014^{\circ}$  per minute. These effects are nearly negligible, but we were careful in the following experiments to keep the temperature of the air constant to a few tenths of a degree; the thermostat was kept, of course, even more constant than this. Conduction through the neck of the flask by way of the walls, the stopper, the thermometer, etc., is evidently of somewhat more consequence than radiation and conduction across the vacuum jacket.

### Heat Capacity Determinations.

The combined heat capacity of the Dewar flask, the contained liquid, the stirrer, thermometer, etc., was determined by the electrical method. The closed container for the ammine was made into a heater for this purpose by winding non-inductively around its enlarged portion a single layer of fine, enameled, copper wire. By closing the lower end of the container and then dipping the whole in boiling asphalt, a thin, but very tough covering was secured for the coil. Indeed, this combination of asphalt and enamel was the only material we discovered which would withstand the joint action of the caustic sodium sulfide solution and the strong heating current. No change in the re-



sistance of the coil could be detected after immersion in the sodium sulfide solution for several hours with the simultaneous passage of a current of several tenths of an ampere.

We did not attempt to maintain an exactly constant current, nor to measure it precisely; instead we kept the current very nearly constant by using a storage battery, a Weston milliammeter and a slide-wire resistance, closed the circuit for a measured interval of time and determined the total quantity of electricity which had passed by means of a silver coulometer.

By this method the heat evolved was obtained from the product of the resistance of the coil and the square of the weight of silver divided by the time; all quantities which could be easily and accurately determined. Since, however, we could secure only copper wire with the requisite enamel coating and copper has the high temperature coefficient of resistance characteristic of pure metals, we were obliged to measure the resistance of the coil during the passage of the heating current under the conditions of the experiment.

For this purpose an additional, open, coil of manganin wire was introduced into the circuit next to the heating coil and immersed in a stirred oil-bath. Two relatively large manganin resistances were then shunted in series around these two coils and the middle points of these two branched circuits were connected through a galvanometer. The large resistance in the ratio arms of this Wheatstone bridge arrangement obviated possible errors due to the heating effect of the current.

It was found that the resistance of the heating coil did increase perceptibly when the current was passed. A curve was constructed connecting current strength and percentage change in resistance and from it such slight corrections as were necessary were applied for the different current strengths employed in the heat-capacity determinations. Moreover, the resistance in each case was corrected to the mean temperature of the determination.

The silver coulometer consisted of a platinum dish cathode and a silver strip anode, so that the current density was kept sufficiently low.<sup>3</sup> The silver nitrate solution contained 40 g. of salt per 100 cc., and a small porous porcelain cup served as an anode diaphragm.

The combined corrections for stirring, radiation and conduction in these heat capacity measurements, as in the subsequent calorimetric experiments, were determined in each case by taking temperature measurements over a long period before and after the heating current was applied. When these readings were plotted, the resulting curves were very smooth and permitted an accurate extrapolation over the heating interval.

Duplicate heat-capacity determinations were made, using as a liquid in the Dewar flask (1) water, (2) a 0.26 *M* solution of sodium sulfide, (3) water containing 8 g. of acido-pentammine chloride in solution and suspension and (4) the same sodium sulfide solution after it had reacted with 8 g. of the same ammine. These were the identical liquids employed in the subsequent calorimetric experiments, and in all the experiments the same volume of liquid (898 cc.) was taken, so that from these measurements, the heat capacity in every calorimetric experiment could be obtained. From the heat capacities of the calorimeter when the ammine was present the heat capacities of the calorimeter containing only the pure liquids can be calculated by subtracting the heat capacity of the ammine. The latter quantity can be calculated with sufficient accuracy for our purpose from the atomic heats of the elements concerned, and amounts to three calories for 8 g.

The results of the heat capacity measurements are given in Table I. The average deviation from the mean of the four values for water and the four values for the sodium

<sup>3</sup> Kohlrausch, "Praktische Physik," B. G. Teubner, Leipzig and Berlin, 8th ed., p. 431.

TABLE I.  
 HEAT CAPACITY OF CALORIMETER.

No.	Liquid.	Time. Seconds.	Resistance. Ohms.	Temperature rise. ° C.	Weight of silver. G.	Total heat cap. Cals.	Heat cap. with H <sub>2</sub> O. Cals.	Heat cap. with Na <sub>2</sub> S. Solution. Cals.
1	H <sub>2</sub> O	1200	55.805	0.739	0.2794	951.9	951.9	...
2		1200	55.692	0.745	0.2804	949.1	949.1	...
3	H <sub>2</sub> O+Am	1200	55.692	0.731	0.2787	955.5	952.5	...
4		1200	55.860	0.743	0.2806	955.8	952.8	...
5	H <sub>2</sub> O+Na <sub>2</sub> S	2160	56.950	0.783	0.3751	918.0	...	918.0
6		1440	51.001	0.890	0.3447	916.2	...	916.2
7	H <sub>2</sub> O+Na <sub>2</sub> S+Am	1260	55.346	0.810	0.2956	918.1	...	915.1
8		1140	55.346	0.766	0.2738	920.6	...	917.6
						Mean	951.6	916.7

sulfide solution is less than 0.2%, which is no greater than the probable error of the experimental data. The mean heat capacities given in this table have been used in all the subsequent calorimetric experiments after applying a small correction for the calculated heat capacities of the added aminnes.

#### Preparation of the Aminnes.

The aminnes were prepared according to the improved methods of Jörgensen,<sup>2</sup> an imported sample of chloro-pentammine cobalt chloride, whose purity had been established by many analyses in this laboratory, serving as the starting material. Repeated analyses of salts prepared by these methods have shown them to have a high degree of purity.

#### Heats of Solution.

The general method of procedure has already been outlined in the section entitled Apparatus and Method. Before the actual determination was begun the stirrer was operated continuously for about an hour to secure a thorough equalization of temperature throughout the apparatus. The stirring was then cut down to 10 seconds before every 2-minute reading for a period of about 30 minutes, after which the ammine was ejected from its container. Continuous stirring was then maintained for a period of 1 minute, and this generally sufficed to bring the greater part of the finely-ground ammine into solution. The stirring was then reduced to its previous rate and continued until a perfectly uniform rate of temperature change had been established. This usually required but 3 or 4, and never more than 10 minutes. The effect of the regular, intermittent stirring was of course corrected for by extrapolation of the resulting curves; a special correction of 0.001° was applied for the one minute of continuous stirring, on the basis of the above preliminary experiments on the effect of stirring. A sample of the curves secured is shown in Fig. 1; the results as a whole are collected in Table II.

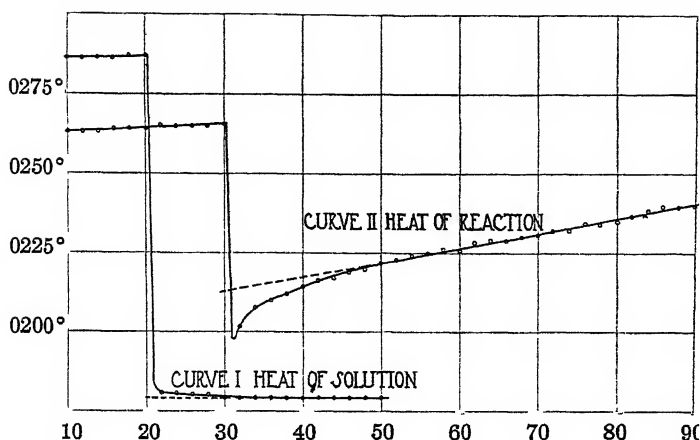


TABLE II.

HEATS OF SOLUTION OF PENTAMMINE COBALT SALTS IN WATER AT 25°.

Pentammine. Salt.	Weight taken. G.	Molar con- cen- tration.	Temperature change.		Heat cap. of sol. cals.	Molar ht. of sol. cals.	Molar ht. of sol. av. cals.
			Observed. ° C.	Corrected. ° C.			
Chloro chloride.....	2	0.00890	-0.105 <sub>5</sub>	-0.106 <sub>7</sub>	950.8	12700	
	2	0.00890	-0.101 <sub>0</sub>	-0.101 <sub>9</sub>	950.8	12140	-12420
Aquo chloride.....	4	0.01661	-0.099 <sub>3</sub>	-0.099 <sub>7</sub>	951.6	6367	
	8	0.03322	-0.203 <sub>3</sub>	-0.205 <sub>1</sub>	953.1	6560	-6460
Bromo bromide.....	1	0.00290	-0.035 <sub>2</sub>	-0.034 <sub>7</sub>	950.3	12660	
	1	0.00290	-0.035 <sub>2</sub>	-0.034 <sub>7</sub>	950.3	12660	-12660
Aquo bromide.....	3	0.00832	-0.073 <sub>0</sub>	-0.073 <sub>0</sub>	950.9	9305	
	3	0.00832	-0.071 <sub>5</sub>	-0.071 <sub>5</sub>	950.9	9114	-9220
Nitrato nitrate.....	2	0.00738	-0.102 <sub>6</sub>	-0.103 <sub>6</sub>	950.9	14800	
	2	0.00738	-0.104 <sub>0</sub>	-0.104 <sub>4</sub>	950.9	15000	-14900
Aquo nitrate.....	5	0.01741	-0.250 <sub>0</sub>	-0.252 <sub>5</sub>	952.3	15400	
	4	0.01393	-0.200 <sub>0</sub>	-0.201 <sub>8</sub>	951.8	15370	-15380

Average deviation of mean  $\pm 200$  cals.

## Heats of Solution Calculated from Solubility Measurements.

Heats of solution are readily calculated from solubility measurements made at different temperatures by use of Van't Hoff's equation. There are difficulties, however, in applying this method to the cobalt ammines. In the first place, time is required for a precise attainment of saturation, and within this period there will be, even at 0°, a conversion of the acido (purpureo) salt into the corresponding aquo(roseo) salt, and *vice-versa*, which will vitiate the solubility measurements. In the second place, to apply Van't Hoff's equation requires a knowledge which we do not possess of the percentage dissociation of the dissolved salt. This latter difficulty can only be avoided in the case of the slightly soluble ammines whose percentage [dissociation is high, and hence can be estimated with

sufficient accuracy from the known percentage dissociation of other salts of the same type.

In view of these difficulties we have only applied this method to chloropentammine cobalt chloride, which is not only but slightly soluble, but also changes more slowly than the corresponding bromo or nitrate amines into the aquo salt. The solubility measurements on this salt were made at three temperatures, 0°, 30°, and 50°, saturation being reached from opposite sides in duplicate experiments. The salt was ground to moderate fineness before use and the suspension was rapidly stirred in a thermostat, but the results at the highest temperature were very discordant, due presumably to partial conversion into aquo salt and to incomplete saturation, and were therefore discarded. At given intervals some of the clear liquid was drawn off through a filter-pipet, its specific gravity was determined and a weighed portion was evaporated to dryness. The ammine was then converted into cobalt sulfate according to Gibbs' procedure<sup>4</sup> and weighed. The results are collected in Table III. It will

TABLE III.  
SOLUBILITY OF CHLORO-PENTAMMINE COBALT CHLORIDE IN WATER.

No.	Temp. °C.	Time. Hours.	Density. t/4°.	Solubility, g. per 100 g. of H <sub>2</sub> O.			Av.	Solubility g. per liter.
				From undersat.	From supersat.	Mean.		
1	0	0.5	1.00096	0.2137	0.2300	0.2219	0.2228	2.244
2	0	1		0.2130	0.2328	0.2229		
3	0	1.5		0.2237	0.2220	0.2228		
4	0	1.5		0.2274 <sup>a</sup>	0.2474 <sup>a</sup>	....		
5	0	3.0		0.2222	0.2229	0.2226		
6	0	3.0	0.9994	0.2215	0.2242	0.2229	0.6088	6.047
7	29.7	0.5		0.6098	0.6070	0.6085		
8	29.7	1.0		0.6091	0.6090	0.6090		
9	50	1.0	0.9945	1.056	1.082	1.069	1.025 <sup>b</sup>	10.01
10	50	2.0		1.110	1.127	1.113		

<sup>a</sup> Not included in taking the mean.

<sup>b</sup> Extrapolated to zero time in view of the evident slight formation of roseo salt.

be seen that the solubilities are concordant and independent of the time, indicating a precise attainment of saturation and a negligible conversion into aquo salt.

The heat of solution was calculated from the data given in Table IV using the equation of Van't Hoff<sup>5</sup> in its differential form where

$$L = RT^2i \left( \frac{d \log_e S}{dT} \right)$$

in which  $L$  represents the molecular heat of solution,  $R$  the gas constant,

<sup>4</sup> Gibbs, "Researches on the Ammonia Cobalt Bases," Smithsonian Contributions to Knowledge, Washington, 1856.

<sup>5</sup> Van't Hoff, *Z. physik. Chem.*, 17, 147 and 546 (1895). See also Noyes and Sammet, *Z. physik. Chem.*, 43, 513 (1903).

$i$  the Van't Hoff coefficient and  $S$  the solubility in grams per liter,  $i$  is the only term for which no immediate data are available; approximate values for it and for  $di/dt$  were obtained on the very generally justified assumption that this salt would resemble, in this respect, the similarly constituted salt, barium chloride;  $i$  and  $di/i dt$  were calculated for barium chloride from the conductivity measurements of Kohlrausch and Gruneisen,<sup>6</sup> and Deguisne,<sup>7</sup> and were found to be 2.610 and  $-0.000038$  respectively at  $25^\circ$ . To evaluate  $d \log S/dt$ , the logarithm of the observed values of  $S$  were plotted against the temperature and were found to lie on a slightly curved line. The equation for the symmetrical parabola passing most nearly through these points was then computed; it was  $\log S = 0.3517 + 0.01657 t - 0.00007054 t^2$ . This equation, when differentiated, gave  $d \log S/dt$  at  $25^\circ = 0.01304$ . Substituting these values, and  $R = 1.985$  cal. per degree and  $T = 298$  in the above equation the result  $L = 13440$  cal. was obtained, which agrees as well as could be expected with the experimentally determined value of  $12400$  cal. This is especially true when one recalls that the calculated value is the *integral* heat of solution,<sup>8</sup> while that experimentally determined is very nearly the *initial* heat of solution, and these will differ somewhat in value except in very dilute solution.

### Heats of Reaction.

The procedure in determining the heats of reaction was practically identical with that followed in the case of the heats of solution, except that a  $0.26 M$  solution of sodium sulfide was used in place of the water. The stirring was made continuous for one minute after the ejection of the ammine and a correction of  $0.001^\circ$  was applied for the extra heating effect. The temperature rise did not usually become uniform until after about 20 minutes; probably the particles of the ammine became coated with a layer of the sulfide. Temperature readings were then continued for some 40 minutes to obtain with certainty the temperature rise per minute. The readings of a typical experiment are plotted in Curve II of Fig. 1. The results of all measurements are collected in Table IV. It will be seen from this table that the average discrepancy between the heat capacities found in duplicate experiments corresponds to an average discrepancy in the temperature change of about  $0.001^\circ$ . It will also be seen that in some cases the reaction is decidedly exothermic, in others endothermic.

<sup>6</sup> Gruneisen, *Sitzber. Ber. Akad.*, 1904, 1215. Landolt-Börnstein-Roth, "Tabellen," 1912, p. 1103.

<sup>7</sup> Deguisne, *Dissertation*, Strassburg, 1895. Landolt-Börnstein-Roth, "Tabellen," 1912, p. 1116.

<sup>8</sup> Roozeboom, *Rec. trav. chim.*, 5, 335-392 (1886); van Deventer and van der Stadt, *Z. physik. Chem.*, 9, 43 (1892).

TABLE IV.

HEATS OF REACTION OF SOLID PENTAMMINE COBALT SALTS WITH SODIUM SULFIDE SOLUTION AT 25°.

Pentammine. Salt.	Weight. G.	Temperature change.		Heat capacity. Cals.	Heat of reaction. Obs. cals.	Heat of reaction Av. cals.
		Obs. °C.	Corrected °C.			
Chloro chloride	7.5475	+0.088 <sub>0</sub>	+0.089 <sub>2</sub>	919.3	2659	2650
	7.5098	±0.087 <sub>0</sub>	+0.085 <sub>8</sub>		2639	
Aquo chloride	8.0000	+0.207 <sub>0</sub>	+0.207 <sub>9</sub>	919.4	6415	6476
		+0.210 <sub>0</sub>	+0.211 <sub>9</sub>		6536	
Bromo bromide	3.0000	+0.007 <sub>0</sub>	+0.005 <sub>1</sub>	917.1	613	635
		+0.007 <sub>5</sub>	+0.005 <sub>6</sub>		657	
Aquo bromide		+0.021 <sub>3</sub>	+0.019 <sub>3</sub>	917.2	2373	2384
		+0.021 <sub>4</sub>	+0.019 <sub>5</sub>		2396	
Nitrato nitrate	2.0000	-0.016 <sub>5</sub>	-0.018 <sub>5</sub>	917.4	-2608	-2560
	6.0000	-0.051 <sub>6</sub>	-0.054 <sub>4</sub>	919.0	-2518	
Aquo nitrate	4.0000	-0.045 <sub>6</sub>	-0.048 <sub>8</sub>	918.0	-3548	-3526
		-0.045 <sub>0</sub>	-0.047 <sub>7</sub>	918.0	-3504	
Average deviation of mean						±30 cal.

By subtracting the heats of solution from the heats of reaction of the solid salts the heats of reaction in solution may be obtained. By subtracting the heats of reaction of the aquo from the corresponding acido salts in solution the heats of transformation are finally obtained. The results of these calculations are collected in Table V.

TABLE V.

HEATS OF REACTION AND TRANSFORMATION OF PENTAMMINE COBALT SALTS IN AQUEOUS SOLUTION AT 25°.

Ammine.	Heat of reaction. Cals.	Heat of transformation. Cals.
Chloro chloride.....	15070	2140
Aquo chloride.....	12930	
Bromo bromide.....	13290	1690
Aquo bromide.....	11600	
Nitrato nitrate.....	12340	480
Aquo nitrate.....	11860	

### Discussion of Results.

The heats of transformation are in reverse order as compared with the velocities of transformation;<sup>1</sup> that is, of the ammines the chloro changes the least rapidly, the bromo next, and the nitrato the most rapidly into the corresponding aquo compound. They follow, in all probability, the same reverse order as compared to the free energy of transformation, although this latter quantity has only been measured in the case of the chloride and bromide. This is of interest, because not only are the magnitude and sign of the heat of transformation the same as has been found for the heats of ionization of salts in water but there, too, the more highly dissociated have, in general, the lesser heats of ionization. All

of these considerations seem then to emphasize the similarity pointed out before between the transformation of the acido (purpureo)-pentammine salts in aqueous solution into the aquo(roseo)-pentammine salts and the electrolytic dissociation of the strong electrolytes in water.

### Summary.

1. A method of calorimetry has been developed in which only observations on a silver coulometer, and of time and electrical resistance are required.

2. It has been shown that the same sulfide of cobalt ( $\text{Co}_2\text{S}_3$ ) is produced by the action of sodium sulfide on chloro- and aquo-pentammine cobalt chloride in aqueous solution.

3. The solubility of chloro-pentammine cobaltic chloride has been measured at several temperatures, and its heat of solution has been computed from these data, and found to be in fair agreement with the directly measured values.

4. The heats of solution in water of a number of acido- and aquo-pentammine cobaltic salts, and their heats of reaction with aqueous solutions of sodium sulfide have been measured. From these data the heats of transformation of the solid acido to the corresponding solid aquo amines have been calculated.

5. The heats of transformation have been found to be antibat to the velocities of transformation, but probably symbat to the free energies of transformation, a reaction similar to that shown by the ionization of salts in water.

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AND NEW YORK CITY.

### NOTE.

**An Interesting Colloid Gel.**<sup>1</sup>—The structure of gels has been a question which has given rise to numerous investigations and we are still far from unanimity of opinion. Probably one of the factors which contributes to the difficulties of the problem is the complexity of the disperse material. Gelatin, for example, has been used in many investigations, but when we realize how inadequate our knowledge is regarding the chemical configuration of the gelatin molecule, and how easily proteins may be altered by physical or chemical factors, it is not surprising that the experimental results have been found to differ widely when different samples of gelatin are used. The same objections apply to agar-agar as apply to gelatin.

Aside from the complex organic substances, such as proteins, gums,

<sup>1</sup> Published with the approval of the Director as Paper No. 263, *Journal Series*, Minnesota Agricultural Experiment Station.

polysaccharides, etc., which show more or less true gel formation, we have silicic acid gels. Here again we have a material of more or less unknown composition. The method of preparing the sodium silicate sol and its past history as well as the concentration of acid by which it is converted into the silicic acid gel all play a part in the properties and behavior of the final gel.

There thus appears to be a need for some substance which can be prepared by anyone in pure form and which will easily set to a rigid gel. We believe that the dibenzoyl derivative of the amino acid *l*-cystine satisfactorily meets all of these requirements.

**Preparation of dibenzoyl-*l*-cystine.**—Two g. of cystine (prepared from human hair by hydrolysis with hydrochloric acid) was suspended in 100 cc. of water, and sufficient 10% sodium hydroxide solution was added to dissolve the amino acid. Ten g. of benzoyl chloride was then added and enough additional sodium hydroxide (in solution) to make a total of 6 g. The mixture was shaken vigorously until all odor of benzoyl chloride had disappeared. Upon acidification with hydrochloric acid the entire solution set to a stiff gel. This was broken up by agitation and thrown upon a Büchner funnel, and the liquid drained off by a strong suction. After filtering for several hours a felt of crystals of the benzoyl derivative remained upon the filter. This was washed with water and recrystallized from somewhat diluted alcohol, yielding long silky needles melting at 180–181° (uncorr.). Brenzinger<sup>2</sup> gives 180–181° (uncorr.) as the melting point of pure benzoyl cystine, whereas Goldmann and Baumann<sup>3</sup> give 156–158°. Undoubtedly 180–181° is the correct value.

*Dibenzoyl cystine is insoluble in water, does not contain water of crystallization and in the crystalline state, at least, has no hydrophilic properties. It is readily soluble in most of the organic solvents and because of the presence of the benzoyl groups it is a relatively strong organic acid.*

At the time we prepared our compound we had not consulted Brenzinger's paper but were relying on the data as given in various texts and handbooks. None of those consulted emphasized the gel-forming property. After we had prepared several samples of benzoyl cystine and had particularly investigated its gel-forming properties, we consulted Brenzinger's paper and found that he had recorded the gel formation. He states that if the alkaline solution of benzoyl cystine prepared from 2 g. of cystine as noted above is diluted to 3 liters before acidification with hydrochloric acid, the resulting mixture will be a rigid gel from which no water can be poured. Assuming a quantitative conversion of the cystine into the benzoyl derivative such a gel would have a concentration of 0.124% of benzoyl cystine.

Undoubtedly this observation of Brenzinger's would have attracted the attention of colloid chemists had it not been published at so early a date. The peculiar gel-forming properties of the substance led us to study it further. We found that we could readily prepare a rigid gel in

<sup>2</sup> Brenzinger, *Z. physiol. Chem.*, **16**, 537 (1892).

<sup>3</sup> Goldmann and Baumann, *ibid.*, **12**, 255 (1888).



which the concentration of the dibenzoyl derivative did not exceed 0.2% and that a gel of 0.1% concentration was rigid enough to hold its shape for a minute or more when the beaker containing the gel was inverted. We believe that these are the most dilute rigid gels that have ever been prepared artificially. Gelatin and silicic acid gels require considerably higher concentrations of the colloid material and even the natural gel in which frog eggs and salamander eggs are embedded and the natural gel of the jelly fish contain more solid material.

**The Preparation of a 0.2% gel.**—Two-tenths g. of pure benzoyl cystine was dissolved in a beaker in 5 cc. of 95% alcohol. While the contents were kept boiling hot, water was added until a volume of 100 cc. had been attained. At this point there was a slight opalescence but no evidence of precipitation or gel formation. The beaker was then covered and set aside to cool. In a short time, usually 2 to 3 hours but occasionally longer, the entire mass had set to a rigid gel comparable to a 5% gelatin gel. In no case was gel formation observed until a considerable period had elapsed after the contents of the beaker reached room temperature.

**Properties of the Gel.**—The gel was practically transparent, no change in opalescence being observed beyond that exhibited by the freshly prepared sol. The gel can be loosened from the walls of the beaker and will support its own weight for a long time. The beaker containing the gel may be left inverted for several hours without breaking the gel. However, in the course of several days some changes take place. The most noticeable one is the formation of opaque nuclei caused apparently by the aggregation of minute stellate groups of needles throughout the gel structure. This phenomenon is accompanied by syneresis or "bleeding" of the gel so that in the course of several weeks most of the benzoyl-cystine has separated in a definitely crystalline condition. When the freshly prepared gel is thrown upon a filter in a Büchner funnel and strong suction is applied, a limpid liquid filters slowly through and the benzoyl cystine remains practically quantitatively on the filter. Usually 8 to 10 hours are required to filter the liquid from 100 cc. of the gel. After filtration the thin "skin" of benzoyl cystine may easily be separated from the filter paper.

**The Structure of the Gel.**—The fact that the benzoyl-cystine may be filtered from the freshly prepared gel by the use of ordinary filter paper and suction argues for a relatively coarse degree of dispersion. Unfortunately we do not have access to a Zsigmondy ultramicroscope so that we are still somewhat in doubt as to the true gel structure. When a portion of the gel is viewed by dark-field illumination,<sup>4</sup> using a 4 mm. objective

<sup>4</sup> Using a Wenham-Sidentopf paraboloid and a special slide similar to that described by Lord (*J. Agr. Res.*, 17, 170 (1919)) with the exception that the cavity in the slide was sufficiently large to allow the insertion of a portion of the gel approximating 5 × 5 mm, surface area and 1 mm. in thickness.

and 12.5 ocular, one observes a fibrillar structure as if the gel were composed of needle crystals of exceedingly small cross section. In fact, the cross section of the fiber is so small as to not be apparent when an oil immersion objective (1.9 mm. fluorite) was used. These fibrillar areas, however, could not be demonstrated to be continuous throughout the gel structure. In certain of our preparations they appeared to be discontinuous and surrounded by an area of approximately equal extent which was optically void. It is possible that the fibers were present in such an area, but we could not demonstrate them with our relatively crude ultramicroscope. Then again the areas in which the fibers could be demonstrated may possibly have been formed by crystal growth following the true gel formation, and may not be essential to the gel structure. Certain of the fibrillar areas apparently grow in opacity and size as the gel ages, serving as nuclei for the crystalline benzoyl-cystine noted earlier. This growth is however to be expected from the Noyes-Nernst rule governing the growth of crystals.

All of the available evidence, however, points to the benzoyl-cystine gel as having a fibrillar structure, the fibrils being exceedingly minute crystals of benzoyl-cystine. The evidence is incomplete, but if 0.2 g. of the non-hydrophilic benzoyl-cystine can form a crystal gel retaining 100 g. of water, such a phenomenon certainly has a profound bearing on the subject of gel formation and gel structure in other systems.

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Received June 10, 1921.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL.]

## THE RELATION BETWEEN THE MODE OF SYNTHESIS AND TOXICITY OF ARSPHENAMINE AND RELATED COMPOUNDS.<sup>1</sup>

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Received June 21, 1921.

In the oldest and probably the most widely used method of preparing arspenamine, 3-nitro-4-hydroxy-phenylarsonic acid is reduced by sodium hydrosulfite directly to arspenamine base which is then converted into the dihydrochloride by solution in methyl-alcoholic hydrochloric acid and precipitated with ether. This procedure has led to wide variations in the toxicity of the product; some preparations kill at doses as low as 60 mg./kg., whereas others do not kill at 130 or 140 mg./kg. Believing that some

<sup>1</sup> This is the fourth of a series of studies on the properties contributing to the toxicity of arspenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general

condition or set of conditions controlled the toxicity, a detailed investigation of the arspenamine synthesis was undertaken. The toxicity discussed in this paper is that described under Type II in a paper by Dr. Reid Hunt<sup>2</sup> and is quite different from that due to the presence of 3-amino-4-hydroxyphenyl-arsenious oxide or to the physical nature of the solution.

The nitrohydroxy acid is obtainable by three commercially feasible processes,<sup>3</sup> and it was found that relatively toxic and nontoxic arspenamine could be obtained from crude or purified nitro acid regardless of the method by which the latter was made. Moreover, the replacement of as much as 5% of the nitro acid by substances which might be present as impurities, *e. g.*, 3,5-dinitro-4-hydroxy-phenylarsonic acid, *o*-nitro-*p*-cresolarsonic acid, or a mixture of 3-nitro- and 5-nitro-2-hydroxy-phenylarsonic acids, caused only slight variations in the toxicity of the resulting arspenamine. In this connection attention should be called to the fact that the presence of the dinitro acid, as an impurity, would lead to the formation of a tri-amino and not a tetra-amino arseno compound as has been suggested. This is a consequence of the formation of an unsymmetrical arseno compound in preference to two symmetrical ones when a mixture of two different arsonic acids is reduced. Previous investigators<sup>4</sup> have mentioned this, and work done in this laboratory is entirely in agreement with that of the others.<sup>5</sup>

Investigation of methods available for the conversion of the base into the dihydrochloride<sup>6</sup> revealed nothing which caused distinct variations in toxicity. In fact, when a sample of the base was converted half into the dihydrochloride by the methyl-alcohol-ether method and half into the dihydrosulfate by precipitation of the latter from a dilute solution of the base in aqueous hydrochloric acid with dil. sulfuric acid the two substances had identical toxicities. In another experiment, the dihydrochloride was dissolved in methyl alcohol and reprecipitated with ether in accordance with the direction of Dr. Reid Hunt, who is also responsible for the biological tests reported in this paper. Additional aid has been received from the Committee of the Permanent Charity Fund, Incorp.

<sup>2</sup> Hunt, *J. Am. Med. Assoc.*, **76**, 854 (1921).

<sup>3</sup> For an outline of these syntheses see Lythgoe, *Chem. Age* (N. Y.), **28**, 390 (1920).

<sup>4</sup> Bertheim, *Chem. Ztg.*, **38**, 756 (1914); Karrer, *Ber.*, **49**, 1648 (1916); Fargher, *J. Chem. Soc.*, **118**, 865 (1920).

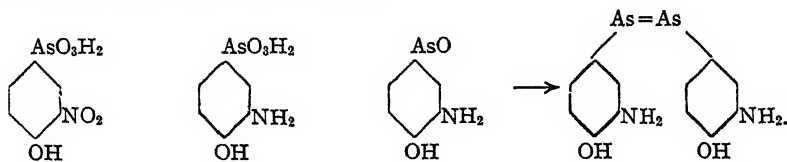
<sup>5</sup> The reduction of equivalent quantities of *p*-hydroxy-phenylarsonic acid and its mononitro or mono-amino derivative gave no acid insoluble arseno compound; the only substance obtained gave a hydrochloride which analyzed for mono-amino-dihydroxy-arsenobenzene hydrochloride. Also, the reduction of equivalent quantities of 3-nitro- or 3-amino-4-methoxy-phenylarsonic acid and 3-amino- or 3,5-dinitro-4-hydroxy-phenylarsonic acid gave no alkali-insoluble arseno compound. These results could be obtained only by the formation of an unsymmetrical molecule.

<sup>6</sup> Ehrlich and Bertheim, *Ber.*, **45**, 756 (1912); Kober, *This Journal*, **41**, 442 (1919).

without any alteration in toxicity. Another portion was converted into the base by treating an aqueous solution with sodium carbonate and the toxicity of the base was equivalent to that of the original hydrochloride.

These results indicate that the toxicity of the arsphenamine is determined during the reduction of the nitrohydroxy acid to arsphenamine base and is not dependent upon the character or source of the nitro compound or upon the conversion of the base into the dihydrochloride.

Examination of the reaction by which arsphenamine base is obtained shows the presence of several known intermediates and the opportunities for undesired side reactions to occur.



At this point in the work the average tolerated dose of a large number of preparations made from the nitro compound by the standard method of reduction was 110 mg./kg.<sup>7</sup> and varied between 70 and 140 mg./kg. When the pure amino acid, from various sources, was reduced under the same set of conditions the arsphenamine consistently had a tolerated dose of 140–150 mg./kg. This figure agrees well with those obtained for arsphenamine prepared from the pure amino acid by other methods<sup>8</sup> and is probably as high as can be attained with any degree of regularity. Hydrosulfite reduction of the pure arsenious oxide gave a product tolerated in doses of approximately 130 mg./kg. It is evident from the wide variations encountered when the nitro acid is the starting material, from the consistency with which an excellent product may be secured by reducing the amino acid by the same method used for the nitro acid, and from the fact that the mechanism of the reaction is the same in both cases after the nitro group has been reduced, that the toxicity of the arsphenamine obtained by hydrosulfite reduction depends upon some variable process in the formation of the amino group. Later, when methods had been developed for the consistent production, from the nitro acid, of arsphenamine with a tolerated dose as low as 50–70 mg./kg., the application of these methods to the reduction of the pure amino acid gave a product with a tolerated dose of approximately 140 mg./kg.

That the toxicity of arsphenamine should be closely bound up with the reduction of the nitro group is not surprising when one considers the many intermediates and by-products encountered in the reduction of nitro compounds. When the quantities of reagents used in this reduction were

<sup>7</sup> The average tolerated dose of the arsphenamine of 6 manufacturers was found by Schamberg, Kolmer, and Raiziss, *Am. J. Med. Sci.*, **160**, 188 (1920), to be 105 mg./kg.

<sup>8</sup> Christiansen, *THIS JOURNAL*, **42**, 2402 (1920); **43**, 370 (1921).

varied no alterations were found in the toxicity of the resulting arspenamine, but as soon as variations were made in the conditions under which the reaction took place marked variations in toxicity were obtained. Ultimately it was determined that the important factors are the degree to which high local concentrations of the nitro compound momentarily exist at the start of the reduction, the temperature at which the nitro group is reduced, and the speed at which the solution, after the reduction of the nitro group, is raised to 55°. When this point in the reaction is reached, the toxicity of the arspenamine which will be produced has been settled. The procedure best suited for the development of low toxicity is very vigorous mechanical stirring while a cold solution of the nitro compound is slowly added to a cold solution of magnesium chloride and sodium hydrosulfite followed by rapid heating to 55°. Obviously the reverse conditions tend to develop high toxicity. That the degree of agitation affects the toxicity only at the time of reduction of the nitro group is shown by the fact that as soon as the color of the nitro group has been destroyed the rate of stirring can be increased to that used for the preparation of arspenamine of low toxicity without decreasing the toxicity of the material.

The influence of each of these conditions is shown in the following table. When nothing is specified it indicates that the importance of the condition had not been discovered and was only approximately constant in successive experiments. All experiments recorded here were conducted identically after 55° had been reached.

TABLE I.  
INFLUENCE OF CONDITIONS OF PREPARATION UPON TOXICITY.

Rate of stirring.	Rate of addition of nitro solution.	Temp. of solutions. ° C.	Rate of heating.	Expt.	Average tol. dose. Mg./kg.	Limit of tol. dose. Mg./kg.	Average as content. %
R <sup>a</sup>	..	..	..	10	110	100-120	30.27
S <sup>b</sup>	..	..	..	3	73	50-100	30.25
R	S	..	..	6	115	100-130	30.99
S	R	..	..	6	73	60-100	30.60
R	S	10	..	9	118	110-130 <sup>c</sup>	30.96
S	R	30	..	9	79	60-90 <sup>c</sup>	29.82
R	S	10	R	5	134	130-150 <sup>d</sup>	31.15
S	R	30	S	2	55	50-60 <sup>d</sup>	29.83

<sup>a</sup> R = Rapid.

<sup>b</sup> S = Slow.

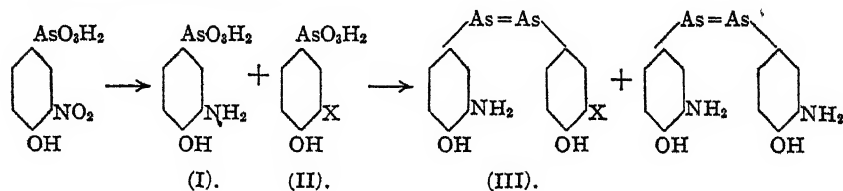
<sup>c</sup> This series includes preparations made: (a) from crude and recrystallized nitro acid made from phenol; (b) from recrystallized nitro acid made from aniline by the oxalyl method; (c) with different commercial brands of hydrosulfite; (d) by different methods of conversion of the base into the dihydrochloride.

<sup>d</sup> This series includes preparations made from crude nitro acid made from phenol and from aniline by the oxalyl method.

Since it has been established that the crucial part of the synthesis lies in the reduction of the nitro group, preliminary work has been done toward ascertaining what undesired secondary process takes place during this reaction. The nitro acid was reduced with hydrosulfite between  $-10^{\circ}$  and  $0$ , in order to slow down this very exothermic reaction and produce conditions similar to prolonged high local concentrations of the nitro compound in the presence of hydrosulfite. The crude amino acid, after isolation, was further reduced with hydrosulfite and yielded arspphenamine tolerated in doses of 120–130 mg./kg. However, when a small quantity of pure amino acid was added to the mother liquor from the crude amino acid separated above and the solution reduced with hydrosulfite, the arspphenamine obtained had a tolerated dose of about 53 mg./kg.; this is the average of 11 experiments in which the tolerated dose varied from 30 to 70. It is evident that the secondary reduction product remains for the most part in the solution when the crude amino acid is isolated. The small quantity of pure amino acid was added to the mother liquor in order that the secondary reduction product may unite, upon reduction, with a molecule of pure amino acid to form the unsymmetrical arseno compound since this is what must happen in the formation of arspphenamine where the ratio of the amino acid to the secondary product is large.

A number of experiments have been made with this solution apparently containing the secondary reduction product and work is now in progress toward the determination of the nature of this product.

The following explanation for the variations found in the toxicity of arspphenamine is suggested.



The toxicity of arspphenamine depends upon the quantity of (III) present, which in turn depends upon the amount of (II) formed at the beginning of the reaction and this is very variable. By regulation of the conditions as discussed above the formation of (II) can be accelerated or retarded but apparently not always entirely inhibited because the average of the best preparations from the nitro acid is below that of preparations from the amino acid. The success of the arspphenamine synthesis is due to the fact that (I) is the major and (II) the minor reduction product.

In order to verify this explanation and to see whether it could be applied to substances related to arspphenamine, mono-, tri-, and tetra- amino dihydroxy-arsenobenzenes were prepared from the nitro and amino acids.

In each case the products prepared by reduction of the amino aryl arsonic acids were less toxic than those prepared from the analogous nitro acids. Interesting biological observations on the effect of increasing the number of amino groups in the hydroxy-arsenobenzene have been made by Drs. Reid Hunt and G. P. Grabfield.<sup>9</sup>

In general the amino arseno compounds vary in toxicity according to the methods of preparation and are obtained in the purest form by reduction of amino arsonic acids. When the nitro acids serve as the starting material more toxic products result owing to the formation of secondary reduction products during the reduction of the nitro group.

The toxicity determinations were made by intravenous injection into white rats and the arsenic determinations by a modification of Lehmann's method.

Fargher and Pyman,<sup>10</sup> in a paper on the "Composition of Salvarsan," showed that arspenamine contains two molecules of water of crystallization and small variable amounts of occluded methyl alcohol. In this laboratory 4 carefully prepared samples of arspenamine base were found to contain the following percentages of arsenic: 37.33, 38.68, 37.78, 38.96; and one sample prepared by precipitation of an aqueous solution of the dihydrochloride with sodium carbonate contained 37.39%. The calculated percentage for  $C_{12}H_{12}O_2N_2As_2$  is 40.98; for 1  $H_2O$ , 39.06; for 2  $H_2O$ , 37.32. Apparently water in variable amounts is firmly attached to the base when the latter forms and is not lost during the drying at room temperature or conversion into the dihydrochloride. If some phenomenon like this did not occur it would be hard to understand how a seemingly dry product when dissolved in anhydrous alcoholic solutions and precipitated with ether could obtain water of crystallization.

In the cases reported in this paper of compounds very closely related to arspenamine the calculated and actual arsenic contents agree well if it is assumed that these substances also have 2 molecules of water of crystallization.

### Experimental.

#### Reduction of 3-Nitro-4-hydroxy-phenylarsonic Acid to Arspenamine.

A. To a solution of 5.3 g. of magnesium chloride hexahydrate in 130 cc. of water at 8°, 30 g. of sodium hydrosulfite is added and a cold (8°) solution of 2 g. of the nitro acid in 46 cc. of water containing 0.66 g. of sodium hydroxide is added gradually during 1-1.5 min. with very vigorous mechanical stirring. One g. of Superfiltchar<sup>11</sup> is added and the mixture is heated to 40° as rapidly as possible and then filtered.<sup>12</sup> The

<sup>9</sup> These observations will be published in a later paper.

<sup>10</sup> Fargher and Pyman, *J. Chem. Soc.*, 117, 370 (1920).

<sup>11</sup> A high grade of vegetable decolorizing carbon, a supply of which was placed at our disposal by the Industrial Chemical Co., N. Y.

<sup>12</sup> Filtering at this point as suggested by Kober, Ref. 6, is of great assistance since it renders the subsequent conversion of the base into the hydrochloride much easier. The carbon helps to remove the more finely divided insoluble matter which often tends to pass through the filter but does not seem to have any bearing upon the toxicity of the arspenamine.

clear colorless filtrate is rapidly heated with stirring to 55° and maintained at 55–60° for 90 minutes. The base is removed by filtration and, after washing and drying *in vacuo* over caustic soda, is converted into the dihydrochloride by dissolving in 7.5 cc., of absolute methyl alcohol containing the calculated amount of dry hydrogen chloride filtering and pouring into 10 volumes of ether<sup>13</sup> cooled to 0–5°. The precipitate is washed with ether and dried *in vacuo* over caustic soda. Yield, 1.2 g. of yellow powder easily soluble in water. Five experiments gave a product which had an average tolerated dose of 130 mg./kg. and arsenic content of 31.15%; that calculated for  $C_{12}H_{14}O_2N_2Cl_2As_2 \cdot 2H_2O$  is 31.58%.

B. The quantities are the same as in A., but the solutions are brought to 30° before mixing, the stirring is very slow when the hydrosulfite and nitro solution are added, and the latter is added in 5 seconds. As soon as the color due to the nitro group disappears the rate of stirring is increased to that used in A and as soon as the hydrosulfite has completely dissolved the material is filtered.<sup>14</sup> The filtrate is heated to 55° during 40 minutes with vigorous stirring and maintained at 55–60° for 1.5 hours. The remaining part of the experiment is like A. The product of 2 experiments gave an average tolerated dose of 55 mg./kg., and arsenic content of 29.82%.

#### Reduction of 3-Amino-4-hydroxy-phenylarsonic Acid.

In this process there is no particular need of careful attention to the details at the beginning as no reaction occurs until the solution has become hot.

To a solution of 5.3 g. of magnesium chloride hexahydrate in 130 cc. of water, 25 g. of sodium hydrosulfite is added with stirring and then a solution of 1.8 g. of the pure amino acid in 40 cc. of water and 5 cc. of saturated sodium carbonate<sup>15</sup> solution. The solution is heated to 30°, filtered, and the experiment is completed as in the other cases. Yield, 1.46 g. of yellow powder easily soluble in water. Four experiments gave a product having an average tolerated dose of 140–150 mg./kg. and arsenic content of 31.55%.

#### Reduction of the Nitro Acid to the Amino Acid.

A solution of 2 g. of the nitro-hydroxy-phenylarsonic acid in 15 cc. of water and 1.5 cc. of sodium hydroxide (sp. gr. 1.295) is cooled in a freezing mixture (–16°) with rapid stirring. At about –2° the sodium salt of the nitro acid separates as fine crystals, with the evolution of heat. When the mush is at about –3°, 5 g. of hydrosulfite is added, the heat generated is partly absorbed as the nitro compound redissolves and if the freezing mixture is efficient the temperature can be kept below 0°. After the color of the nitro group has disappeared the temperature falls to –10°, and the amino acid starts to separate. At the end of ½ hour 0.6 cc. of glacial acetic acid is added and the material is left in the ice box for 1 hour. After filtration, washing, and air-drying, 1.2 g. of the crude amino acid is obtained.

The mother liquor is treated with 1.5 cc. of sodium hydroxide, and a solution of 0.5 g. of pure amino acid in 10 cc. of water and 1.5 cc. of saturated sodium carbonate solution is added. This solution is added to one of 2.6 g. of magnesium chloride hexahydrate in 20 cc. of water to which 11 g. of hydrosulfite has been added. The reduction and conversion of the base into the dihydrochloride is carried out as in the case of the pure amino acid. The average of the products from 9 experiments is 0.2 g. of brownish-yellow powder which dissolves very readily in water and is tolerated in doses of 53 mg./kg.

<sup>13</sup> Absolute ether is unnecessary.

<sup>14</sup> Carbon is not necessary as the fine particles coagulate rapidly at this temperature and are easily filtered out.

<sup>15</sup> Sodium carbonate is used in place of hydroxide as the aminohydroxy acid oxidizes much less rapidly in the carbonate solution.



Reduction of the crude amino acid by the method used for the pure acid gives 1.3 g. of arspphenamine with a tolerated dose of 120 mg./kg. or above and an arsenic content of 31.05%.

### 3-Amino-4,4'-dihydroxy-arsenobenzene Hydrochloride.

I. A mixture of 0.9 g. of anhydrous monosodium *p*-hydroxy-phenylarsonate and 0.9 g. of 3-amino-4-hydroxy-phenylarsonic acid is reduced by the method used in preparing arspphenamine from the amino acid. One and one-tenth g. of base is obtained which is completely soluble in acids. When a filtered methyl-alcoholic solution of the hydrochloride is poured into ether an oily substance separates which after decantation of the ether is dissolved in water and precipitated by pouring into 1:1 hydrochloric acid. After filtering, washing with acid and drying *in vacuo* over caustic soda, 0.7 g. of reddish-orange powder is secured which is soluble in water and is tolerated in doses above 130 mg./kg.

*Analysis.* Calc. for  $C_{12}H_{12}O_2NCIAs_2 \cdot 2H_2O$ : As, 35.43. Found: 35.39.

II. A mixture of 0.9 g. of monosodium *p*-hydroxy-phenylarsonate and 1 g. of 3-nitro-4-hydroxy-phenylarsonic acid is reduced by Method A used to prepare arspphenamine from the nitro acid but without using carbon, without particularly rapid heating to 55°, and filtering at 30° instead of 40°. <sup>16</sup> One g. of tan colored base is obtained. By dissolving it in 30 cc. of water and 0.3 cc. hydrochloric acid (sp. gr. 1.19) and pouring the filtered and cooled solution into 60 cc. of cold 1:1 hydrochloric acid the hydrochloride is precipitated. Continuing as in Procedure I one obtains 0.9 g. of reddish-orange solid, the tolerated dose of which is 120 mg./kg., and whose arsenic content is 36.12%.

III. The mixture of nitrohydroxy and hydroxy acids is reduced by Method B for the preparation of arspphenamine from the nitro acid but the filtered solution is not heated particularly slowly to 55°. The hydrochloride is obtained as above. Yield: 0.8 g. of reddish-orange solid which is tolerated in doses of 80 mg./kg. and has an arsenic content of 35.98%.

In each of the following experiments the arseno base is converted into the hydrochloride by the methyl alcohol-ether method used for arspphenamine.

### 3,5,3'-Tri-amino-4,4'-dihydroxy-arsenobenzene Trihydrochloride.

I. A mixture of 0.9 g. of 3-amino-4-hydroxy-phenylarsonic acid and 0.95 g. of 3,5-diamino-4-hydroxy-phenylarsonic acid is reduced by the method used to reduce the mono-amino acid to arspphenamine. Yield, 1.5 g. of yellow powder which is very readily soluble in water and is tolerated in doses of 80 mg./kg.

*Analysis.* Calc. for  $C_{12}H_{10}O_2N_3Cl_3As_2 \cdot 2H_2O$ : As, 28.49. Found: 28.68.

II. A mixture of 1 g. of 3-nitro-4-hydroxy-phenylarsonic acid and 1.17 g. of 3,5-dinitro-4-hydroxy-phenylarsonic acid is reduced as in Preparation II of the mono-amino dihydroxy-arsenobenzene. Yield, 1.2 g. having a tolerated dose of 80 mg./kg. and an arsenic content of 28.23%.

III. The above mixture of mono- and dinitro acids is reduced as in Preparation III of the mono-amino-dihydroxy-arsenobenzene. Yield, 1.15 g.; tolerated dose, 60 mg./kg.; arsenic content, 28.70%.

### 3,3',5,5'-Tetra-amino-4,4'-dihydroxy-arsenobenzene Tetrahydrochloride.

In the following experiments only that portion of the base soluble in methyl alcoholic hydrochloric acid<sup>17</sup> was used.

<sup>16</sup> This work was done before the influence of the rate of heating had been investigated.

<sup>17</sup> Raiziss and Gavron, *THIS JOURNAL*, 43, 582 (1921).

I. One and nine-tenths g. of 3,5-diamino-4-hydroxy-phenylarsonic acid is reduced by the method used in reducing the mono-amino acid to arsphenamine. Yield, 0.6 g. yellow powder which is very easily soluble in water and which is tolerated in doses of 70 mg./kg.

*Analysis.* Calc. for  $C_{12}H_{13}O_2N_4Cl_4As_2 \cdot 1H_2O$ : As, 26.78; calc. for  $2H_2O$ : 25.95. Found: 27.29.

II. Two and three-tenths g. of 3,5-dinitro-4-hydroxy-phenylarsonic acid is reduced as in Preparation II of the mono-amino analog. Yield, 0.4 g.; tolerated dose, questionable at 50 mg./kg.; arsenic content, 25.55%.

III. The dinitro acid is reduced as in Preparation III of the mono-amino analog. Yield, 0.4 g.; tolerated dose, 50 mg./kg.; arsenic content, 26.10%.

### Summary.

1. It has been proved that the toxicity of arsphenamine prepared by hydrosulfite reduction of 3-nitro-4-hydroxy-phenylarsonic acid is determined during the reduction of the nitro group.

2. By altering the conditions under which the nitro group is reduced the toxicity of the arsphenamine can be made to fluctuate between wide limits. Two sets of conditions have been determined which enable one to produce arsphenamine of widely different toxicity; one set results in a tolerated dose of 130 mg./kg. and the other of 55 mg./kg.

3. For the consistent production of arsphenamine of the lowest toxicity it is advisable to use pure 3-amino-4-hydroxy-phenylarsonic acid as the starting material.

4. It appears to be general that the amino aryl arseno compounds vary in toxicity with the method of preparation and are obtained in the least toxic condition by the reduction of amino arsonic acids. Due to the formation of by-products during the reduction of the nitro group, more toxic products result if the nitro acids serve as the starting material. These secondary reduction products unite with the amino acid in the subsequent reduction of the arsonic acid group to form unsymmetrical arseno compounds.

I take this opportunity to thank Dr. Reid Hunt for his kindness in determining the toxicity of the large number of samples involved in this work, and Miss Helen A. Pratt for her careful work in preparing some of the intermediates used.

BOSTON, MASSACHUSETTS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

**CHLORINATION AND THE FORMATION OF CHLORO-AMINES  
BY MEANS OF NITROGEN TRICHLORIDE.<sup>1</sup>**

BY GEORGE H. COLEMAN WITH WILLIAM ALBERT NOYES.

Received June 27, 1921.

**Introduction.**

The investigation was first undertaken in the hope that it might have a bearing on the general question of the positive and negative character of atoms in combination.

A study of the reaction between nitrogen trichloride and ethyl bromide was made with the thought that it might yield triethylamine and free chlorine and bromine, or perhaps a chlorobromine compound. A reaction of this kind would, of course, be of much interest in relation to the general problem. Ethyl iodide was first used, but it was found very difficult to control the reaction. The work was therefore carried out with ethyl bromide.

No evidence was found of the formation of an amine. The products of the reaction were ammonium chloride, nitrogen, chlorine, bromine, and a small amount of a high-boiling liquid residue left upon distillation of the ethyl bromide. That the nitrogen trichloride did act as a chlorinating agent to a slight extent was evidenced by an analysis of the three principal fractions of the high-boiling residue. The results seemed to indicate that these products were not the same as those found when Lescoeur<sup>2</sup> studied the action of chlorine on ethyl bromide.

To determine whether or not nitrogen trichloride differs from free chlorine in its chlorinating action, the investigation was continued. Ethyl chloride was used in place of ethyl bromide in order to simplify the identifications of the products.

With the thought of extending the work to a different class of compounds, the reaction of nitrogen trichloride was also tried with toluene, with benzene, and with benzyl chloride. In each case, a very unexpected result was obtained in that, along with other products of the reaction, small amounts of chlorinated amines were formed.

**Theoretical.**

**I. Chlorination.**—The work with nitrogen trichloride and ethyl chloride was carried out as that with the ethyl bromide had been, without exposure to light other than dim artificial light. The products of the

<sup>1</sup> Abstract of a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Lescoeur, *Bull. soc. chim.*, 29, 483 (1878).

reaction were similar to those obtained with the ethyl bromide. The most interesting and significant feature of the work with this compound, however, was the fact that, in addition to the usual products of the action of chlorine on ethyl chloride, the high-boiling residue contained a relatively large amount of ethylene chloride.

It has been quite well established that ethylene chloride is not a product of the chlorinating action of free chlorine on ethyl chloride in the absence of a catalytic agent. As the products of this reaction, Regnault<sup>3</sup> found ethylidene chloride, together with several higher chlorinated derivatives of ethane, but no ethylene chloride. Damoiseau,<sup>4</sup> although his experiments were performed at a higher temperature, found no ethylene chloride. Geuther<sup>5</sup> apparently found traces of ethylene chloride in his product, but thought it was due to impurities in the ethyl chloride used. Städel<sup>6</sup> prepared 5 kg. of the reaction product, which on careful fractionation, gave no evidence of ethylene chloride. Denzel<sup>7</sup> also secured the same result. However, Victor Meyer and Müller<sup>8</sup> did prepare ethylene chloride from ethyl chloride by heating equivalent amounts of antimony pentachloride and ethyl chloride at 100° in sealed tubes. They also prepared ethylene bromide from ethyl bromide and bromine, with iron filings as a catalytic agent.

As mentioned above, the work with the aromatic compounds was undertaken with the thought of studying the chlorinating action of nitrogen trichloride on a different class of substances. In the case of toluene, it was found that the high-boiling residue left on distillation of the toluene consisted of a mixture of monochloro-toluenes and benzyl chloride together with higher chlorinated products. Hentschel<sup>9</sup> found benzene hexachloride as the product of the action of nitrogen trichloride on benzene in the sunlight. It might be pointed out in this connection that sunlight decomposes nitrogen trichloride rapidly. Probably this product was formed by the action of free chlorine on the benzene. Benzene hexachloride was also found to be the main chlorination product of the trichloride with benzene in this investigation. Although in most cases, the reaction was carried out in the dark, an excess of chlorine was present in the solution soon after its preparation, as a result of the decomposition of the trichloride.

**II. Chloro-amines.**—In all the reactions studied, a white precipitate containing ammonium chloride was formed. In the case of toluene, of benzene and of benzyl chloride, when this white precipitate was dissolved in water and an alkali was added, a mixture of insoluble amines separated at once. With benzene and with benzyl chloride, the white precipitate

<sup>3</sup> Regnault, *Ann. Chem. Pharm.*, **33**, 312 (1840).

<sup>4</sup> Damoiseau, *Compt. rend.*, **63**, 60 (1876).

<sup>5</sup> Geuther, *Z. Chem.*, **7**, 147 (1871).

<sup>6</sup> Städel, *Ann.*, **195**, 182 (1879).

<sup>7</sup> Denzel, *ibid.*, **195**, 204 (1879).

<sup>8</sup> Victor Meyer and Müller, *Ber.*, **24**, 4249 (1891).

<sup>9</sup> Hentschel, *Ber.*, **30**, 1436 (1897).

was found to contain the hydrochlorides of the amines only when the solutions had been exposed to sunlight, or after it stood for a long time. But, in all cases, if the solutions from which the precipitate had been removed were shaken with conc. hydrochloric acid, amines were found in the aqueous solution.

The properties of this intermediate compound present in the original solutions are illustrated in the work with benzene. It was found that it did not possess basic properties and was not easily hydrolyzed or reduced. When it was shaken with conc. hydrochloric acid, free chlorine was liberated and aniline derivatives were formed. This intermediate compound is probably an N-chloro-amine, *i. e.*, a chloro-amine in which the chlorine is combined with the nitrogen.

The work of Bender<sup>10</sup> is typical of that done by several investigators on the preparation and rearrangement of N-chloro-amines or substituted nitrogen chlorides. N-chloro-acetanilide was prepared from acetanilide and calcium hypochlorite. When heated to 172°, this compound rearranged to give *p*-chloro-acetanilide. In a study of the characteristic rearrangements of the substituted nitrogen halides, Chattaway and Orton<sup>11</sup> prepared a series of compounds in which the halogen of a chloro- or bromo-amine,  $C_6H_5NRX$ , rearranged successively to compounds with the halogen in positions 4, 2 and 6. The chloro-amine  $C_6H_5X_3NRX$ , which was finally obtained did not undergo further rearrangement.

The action of nitrogen trichloride on aniline, on methyl aniline and on dimethyl aniline has been studied by Hentschel.<sup>12</sup> When equimolecular parts of aniline and a solution of nitrogen trichloride in benzene react, trichloro-aniline is formed. This compound may also be formed by passing chlorine into a suspension of aniline hydrochloride in benzene. Methyl aniline similarly gives trichloro-methylaniline. Dimethyl aniline gives a product the structure of which was not determined.

Beilstein and Kurbatow<sup>13</sup> have prepared trichloro-aniline and tetrachloro-aniline by chlorination of mono and dichloro-aniline. Pentachloro-aniline has been prepared by Langer<sup>14</sup> by passing chlorine into an ether solution of dichloro-aniline.

Without introducing the question of positive and negative valence, it may be suggested as a possible explanation of the mechanism of the formation of the amines that the nitrogen trichloride adds to the benzene ring to give a compound,  $C_6H_5NCl_2.Cl$ . This may be followed by the loss of hydrochloric acid to give a chloro-amine,  $C_6H_5NCl_2$ . A possible explanation of the transformation produced by conc. hydrochloric acid may be the following. One molecule of hydrochloric acid adds to the nitrogen and is followed by the loss of a molecule of chlorine. This would leave an N-monochloro-amine which by a similar process is changed to the true amine.

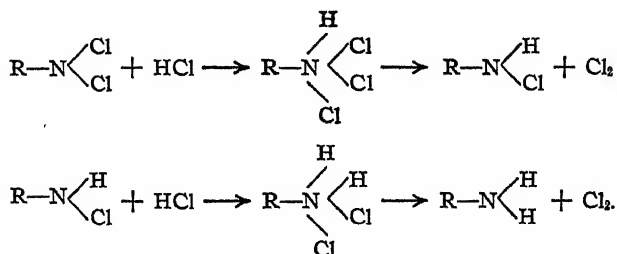
<sup>10</sup> Bender, *Ber.*, 19, 2272 (1886).

<sup>11</sup> Chattaway and Orton, *Ber.*, 32, 3572 (1899).

<sup>12</sup> Hentschel, *Ber.*, 30, 2643 (1897).

<sup>13</sup> Beilstein and Kurbatow, *Ann.*, 196, 230 (1879).

<sup>14</sup> Langer, *ibid.*, 217, 120 (1882).



One of us<sup>15</sup> has shown that nitrogen trichloride and hydrochloric acid yield ammonium chloride and chlorine quantitatively, even in the absence of water. A similar explanation of the mechanism of the reaction was given.

The amines were extracted with ether after the addition of alkali to the aqueous solutions, and subsequently studied. From the method of formation and the presence of an excess of chlorine in the solutions a mixture of chlorinated amines was to be expected. This proved to be the case, the products evidently consisting of mixtures of chlorinated anilines and toluidines, respectively. These products when first obtained by evaporation of the ether from a dry ether solution, were viscous liquids. In the case of the product from benzene, a crystalline substance was obtained by recrystallization from ether and ligroin. The toluene product behaved quite peculiarly in that, on standing a few days, it changed to a dark brittle rosin-like solid. The amine mixture obtained from benzene did not do this. If chlorine had substituted in the side chain of the toluene molecule, such a change could be explained by a reaction between the chlorine of one molecule and the amino group of another. With this in mind, the action of nitrogen trichloride on benzyl chloride was tried. The viscous liquid mixture of amines obtained from this reaction solidified in a few days as that from toluene had done. The explanation given then seems probable.

### Experimental.

**I. Nitrogen Trichloride and Ethyl Chloride.**—Various methods for the preparation of nitrogen trichloride were tried. The method which was most satisfactory and the one finally used was the following. A solution of ammonium sulfate or ammonium nitrate, together with a suitable solvent for the nitrogen trichloride (in this case ethyl chloride itself was used), was surrounded with a freezing mixture at  $-10^\circ$  to  $-20^\circ$ , and the chlorine was passed into this solution at the rate of 0.2 to 0.4 g. per minute. The solutions were kept in intimate contact by means of a stirrer operated by a small motor. When the reaction was complete, the ethyl chloride solution was separated from the aqueous layer and dried with calcium chloride. Samples were taken and the remainder of the solution was sealed in thick-walled glass tubes and left in the dark for from 10 to 20 days.

<sup>15</sup> Noyes, *THIS JOURNAL*, **42**, 2173 (1920).

In the analysis of the solutions, the nitrogen was determined with conc. hydrochloric acid, according to the reaction  $\text{NCl}_3 + 4 \text{HCl} = \text{NH}_4\text{Cl} + 3 \text{Cl}_2$ , a method developed by one of us<sup>16</sup> and found to give better results than the usual sodium sulfite reduction. The ammonia was then determined by distillation from an alkaline solution. The chlorine was determined in another sample by Volhard's method, after it was reduced with sodium sulfite and treated with just enough potassium permanganate to oxidize the excess of sulfite.

In all, 1105 g. of solution containing 504.4 mg. atoms of nitrogen was prepared and used. From this amount the high-boiling residue formed in the reaction, on careful fractionation, gave the following fractions.

TABLE I.  
FRACTIONATION OF HIGH-BOILING RESIDUE.

Temp. ° C.	Vol. Cc.	Temp. ° C.	Vol. Cc.
50-58	0.25	81-84	1.00
58-62	0.50	84-150	0.20
62-72	0.40	150-175	0.50
72-76	0.20	175-190	2.00
76-81	0.25	Residue above 190°, 0.70	

Several of the usual methods for distinguishing between ethylene chloride and ethylidene chloride were tried with the known substances, but with the very small amounts with which it was necessary to work in the case of the fractions obtained above, none of these was found to be satisfactory. Finally a method of differentiation was developed in which very small quantities could be used. This was based on the rates of hydrolysis of the two chlorides by alkali, followed by oxidation of the product of hydrolysis with alkaline permanganate and the determination of the oxalate formed by titration with standard permanganate in hot acid solution. Ethylidene chloride was found to hydrolyze more rapidly than ethylene chloride and to give very much less oxalate on oxidation. The titration for 0.2 cc. each of ethylene and ethylidene chloride took 20.08 cc. and 3.05 cc. of standard permanganate solution respectively. The fractions of the chlorinated product corresponding to the boiling points of ethylene and ethylidene chloride behaved in every way like those of the known substances. The 81-84° fractions required 18.00 cc. of permanganate solution for oxidation of the oxalate formed, the 58-62° fraction, 3.90 cc. only.

**II. Nitrogen Trichloride with Toluene and with Benzyl Chloride.**—The solutions of the trichloride in toluene and the other aromatic liquids were prepared in much the same way as those in ethyl chloride had been. Five solutions in toluene were prepared totaling 1706 g. of solution and containing 921.7 mg. atoms of nitrogen and 2633.5 mg. atoms of chlorine. The ratio of chlorine to nitrogen is 2.85. After preparation the solutions gradually became opalescent and in the course of 5 or 6 hours, quite warm. In 12 to 15 hours the reaction was evidently complete, unless the solution had been kept cool. In that case, 3 or 4 days were required. The white precipitate which formed in the toluene solution was found to be a mixture of ammonium chloride and the hydrochloride of the amines. From a solution containing 114 mg. atoms of nitrogen, about 1 g. of free amine was found in the white precipitate and about an equal amount was secured from the toluene solution by treatment with conc. hydrochloric acid. Thus, only a small percentage of the total nitrogen present in the original solution was found in the amines. Of the remainder, about  $\frac{3}{4}$  was evolved as free nitrogen and  $\frac{1}{4}$  formed ammonium chloride. The toluene solution from the 5 preparations was found to contain 8 to 10 g. of the monochloro-toluenes, and 10 to 12 g. of benzyl chloride, with a

<sup>16</sup> Noyes, *THIS JOURNAL*, **42**, 2178 (1920).

large residue boiling above  $190^{\circ}$ . These fractions were identified by boiling point and other properties.

In the study of the amines some of the tests made were the following. By the sodium-fusion method the substance was found to contain nitrogen and chlorine. When a sample was diazotized and mixed with an alkaline solution of  $\beta$ -naphthol, a bright reddish-yellow precipitate was formed. Carbon dioxide was passed into a dry ether solution, but no amine carbonate was precipitated, proving the absence of benzyl amine,  $C_6H_5CH_2NH_2$ . The isocyanide test indicated the presence of a primary amine. The reaction with benzene sulfonyl chloride also showed this. When some of the free amine product was boiled with ammonium hydroxide, chlorine was found to be present in the solution. When the liquid mixture of the free amines stood for a few days, it slowly changed to a hard, brittle solid.

When dry hydrogen chloride was passed into an anhydrous ether solution of the amines the hydrochlorides were readily formed as a white precipitate. The molecular weight was determined by solution in dil. nitric acid and precipitation of the chloride as silver chloride. Assuming the presence of only one amino group in the molecule this gave a molecular weight of 273.5. A nitrogen determination of the hydrochloride by the absolute method gave 5.04% of nitrogen. This agrees quite closely with the theory that the molecule contains but one amino group. The hydrochloride of tetrachloro-toluidine contains 4.98% of nitrogen; that of trichloro-toluidine 5.69%.

Calc. for  $C_7H_7Cl_4NH_2HCl$ : Cl, 63.1; Calc. for  $C_7H_5Cl_3NH_2HCl$ : Cl, 57.5. Found: Cl, 59.0.

The only important features of the work with benzyl chloride were the following. The reaction occurred much more slowly. No amine was found in the white precipitate, unless the solution had been exposed to sunlight, or allowed to stand a long time. The viscous liquid product gradually solidified as that from toluene had done.

**III. Nitrogen Trichloride and Benzene.**—The solutions were prepared in the usual way. This reaction took place much more slowly than did the reaction with toluene. The main chlorination product was benzene hexachloride. The white precipitate contained no amine, unless the solution was allowed to stand a long time or had been exposed to sunlight. The benzene solution from which the precipitate had been removed was shaken with enough sodium sulfite solution to remove any free chlorine. No amine, or at most only a trace, was found in the sulfite solution. The benzene solution did not now have the yellow color of free chlorine, nor did it liberate iodine from potassium iodide readily, as a solution of chlorine would, but only on prolonged shaking. This nearly colorless benzene solution was then shaken with conc. hydrochloric acid. The benzene turned yellow and readily liberated iodine from potassium iodide, and the aqueous layer was found to contain the amines. It was found that the benzene solution of this N-chloro-amine could be concentrated by vacuum distillation.

The amount of the amine mixture obtained was about the same as that from toluene. Most of the tests made with the amines from toluene were carried out with this product. A mixture of chloro-anilines was indicated. The viscous liquid mixture of the free amines did not solidify on standing; but on treatment with ether and ligroin gave a crystalline product. The hydrochloride was made by passing dry hydrogen chloride into an anhydrous ether solution. A molecular weight determination with this material gave 287. The molecular weight of the hydrochloride of tetrachloro-aniline is 287.5, and of pentachloro-aniline, 303.

### Summary.

1. Nitrogen trichloride reacts with ethyl chloride to give, among other products, ethylene chloride. This compound is not a normal product of



the action of free chlorine on ethyl chloride in the absence of a catalytic agent.

2. Nitrogen trichloride with toluene forms benzyl chloride and the monochloro-toluenes together with higher chlorinated derivatives.

3. With benzene the main chlorination product is benzene hexachloride.

4. With toluene, with benzene, and with benzyl chloride, nitrogen trichloride forms small amounts of N-chloro-amines.

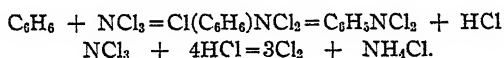
5. The N-chloro-amine group of the compounds formed from toluene and benzyl chloride is located in the nucleus and not in the side chain.

6. The chloro-amines at first formed are acted upon further by the nitrogen trichloride, or by chlorine, to give chlorinated chloro-amines. From benzene, the ultimate product is probably C-pentachloro-N-dichloro-aniline  $C_6Cl_5NCl_2$  but such a compound was not isolated.

7. The chlorinations referred to take place at ordinary temperatures, and consequently are different from the rearrangements of chloro-amines studied by Chattaway and Orton.<sup>11</sup> In this regard and also because all of the hydrogen atoms of the benzene nucleus may be replaced by chlorine, they resemble the chlorination of aniline hydrochloride by chlorine.<sup>14</sup>

8. The C-chloro-N-chloro-aniline liberates chlorine on treatment with conc. hydrochloric acid and is converted to C-chloro-aniline.

9. The facts established are most easily explained by assuming that the reactions are represented by the following equations.



10. The free chlorine from the last reaction would then chlorinate the chloro-amine.

11. The formation of hydrochloric acid under 9 involves a change of positive chlorine to negative, and the formation of considerable quantities of free nitrogen may be connected with this change.

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS,  
NORTHWESTERN UNIVERSITY.]

## 7-CHLORO-7,12-DIHYDRO- $\gamma$ -BENZO-PHENARSAZIN AND SOME OF ITS DERIVATIVES.<sup>1</sup>

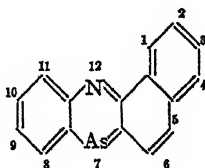
By W. LEE LEWIS AND C. S. HAMILTON.

Received June 27, 1921.

Of the nuclear heterocyclic arsenic compounds, that is, containing arsenic in the ring, those resulting from the condensation of arsenic chloride with diphenyl ether,<sup>2</sup> and with diphenylamine<sup>3</sup> together with their respective derivatives have been described. The German patent mentions the similar compounds formed with  $\beta,\beta$ -dinaphthylamine,  $p$ -ditolylamine,  $\alpha,\alpha$ -dinaphthylamine and  $p$ -oxy-diphenylamine, but the products or their derivatives are not described. Grüttner and Wiernik<sup>4</sup> prepared phenyl-arsino-pentamethylene and Grüttner and Krause<sup>5</sup> phenyl-arsino-tetramethylene. Of the heterocyclic arsenical compounds containing two nuclear arsenic atoms, arsanthren or diphenylene-diarsin and its derivatives have been prepared by Kalb.<sup>6</sup>

This investigation had for its purpose the preparation of additional compounds of this type, particularly those resulting from the condensation of arsenic trichloride with diphenyl methane, benzophenone, its oxime, diphenyl sulfide, diphenylhydrazine and phenyl- $\alpha$ -naphthylamine. Results were negative except with diphenyl-hydrazine which yielded 6-chloro-phenarsazin, and phenyl- $\alpha$ -naphthylamine which yields 7-chloro-7,12-dihydro- $\gamma$ -benzo-phenarsazin.

The hypothetical parent compound for the following derivatives would be  $\gamma$ -benzo-phenarsazin.



It is interesting to note that the 7-chloro derivative is much less irritating physiologically than the corresponding diphenyl-chloro-arsine,

<sup>1</sup> This work was done under a grant from the Interdepartmental Social Hygiene Board, Washington, D. C., Dr. T. A. Storey, Secretary. Some of the water-soluble products are being tested by Dr. A. S. Loevenhart of the University of Wisconsin, for their pharmaceutical value.

<sup>2</sup> Lewis, Lowry and Bergeim, *THIS JOURNAL*, **43**, 891 (1921).

<sup>3</sup> A. Contardi, *Giorn. chim. applicata*, **2**, 100 (1920); *C. A.* **14**, 2628 (1920); Ger. pat. 281049, Friedländer, **12**, 843; Wieland, *Ann.*, **423**, 1 (1921).

<sup>4</sup> Grüttner and Wiernik, *Ber.*, **48**, 1479 (1915).

<sup>5</sup> Grüttner and Krause, *ibid.*, **49**, 440 (1916).

<sup>6</sup> Kalb, *Ann.*, **423**, 39 (1921).

6-chloro-phenarsazin or 6-chloro-phenoxarzin. Moreover, it possesses to a marked degree the property, not shown by the others, of forming stable alkoxy derivatives of the type  $>As-OR$ .<sup>7</sup> The series of derivatives from methoxy to *n*-butoxy, not including the *iso*-propoxy which apparently forms with great difficulty, also the phenoxy and benzyloxy, are here described. These compounds are formed by adding in excess the respective alcohols treated with metallic sodium to a hot xylene solution of 7-chloro-7,12-dihydro- $\gamma$ -benzo-phenarsazin. The excess of sodium alcoholate and the resulting sodium chloride are removed by filtration and the filtrate concentrated to crystallization. The products are all recrystallizable from hot xylene, and have sharp melting points ranging from 209° to 152° (uncorr.). They are attacked by 10% sodium hydroxide solution setting free the alcohol. They are all soluble in carbon tetrachloride, glacial acetic acid and acetone which are good recrystallizing agents. An alcohol other than that corresponding to the alkoxy group present cannot be used for purification as replacement of the alkyl results. Similarly, attempted recrystallization of an alkoxy derivative with aqueous phenol gives the phenoxy compound.

### Experimental.

7-Chloro-7,12-dihydro- $\gamma$ -benzophenarsazin,  $HN \begin{matrix} \diagup C_{10}H_5 \\ \diagdown C_6H_4 \end{matrix} AsCl$ .—Eighty-eight g.

of phenyl- $\alpha$ -naphthylamine and 80 g. (10% excess) of redistilled arsenic trichloride were heated under a reflux condenser. The mixture commenced to boil at 165–170° with evolution of hydrogen chloride. The boiling temperature gradually rose to 200° when the evolution of hydrogen chloride had practically ceased. The time required to reach this temperature was about 2 hours. Upon cooling the reaction mixture solidified to a greenish-yellow mass. The yield of the crude product was 115 g., 87% of the calculated amount. The crude product was recrystallized from xylene and washed with alcohol. A second recrystallization from xylene yielded fine needles, canary-yellow in color and melting at 219° (uncorr.).

7-Chloro-7,12-dihydro- $\gamma$ -benzophenarsazin is insoluble in water and is not attacked by 6 *N* sodium hydroxide solution. It is soluble in xylene, glacial acetic acid, alcohol, benzene, and carbon tetrachloride, and has a slightly irritating effect on the mucous membranes of the nose and throat. The best solvent for recrystallization is xylene in which it is 5% soluble.

*Analyses.* Subs., 0.1995, 0.2018: 15.88, 16.20 cc. of 0.0765 *N* iodine sol. Calc. for  $C_{16}H_{11}NClAs$ : As, 22.90. Found: 22.83, 23.07.

Subs., 0.1544, 0.1756: AgCl, 0.0655, 0.0786. Calc. for  $C_{16}H_{11}NClAs$ : Cl, 10.82. Found: 10.48, 11.05.

7-Methoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin,  $HN \begin{matrix} \diagup C_{10}H_5 \\ \diagdown C_6H_4 \end{matrix} As-OCH_3$ .—Sodium

methylate, prepared by dissolving 1.4 g. of clean metallic sodium in 50 cc. of absolute methyl alcohol, was added to 9 g. of 7-chloro-7,12-dihydro- $\gamma$ -benzophenarsazin

<sup>7</sup> Cf. Michaelis, *Ann.*, 321, 143 (1902); Wieland and Rheinheimer, *Ann.*, 423, 1 (1921).

dissolved in 200 cc. of hot xylene. The mixture was heated under a reflux condenser for 10 minutes. The excess of sodium methylate and the sodium chloride produced in the reaction were filtered hot. Upon cooling, the filtrate remained clear. Approximately 100 cc. of xylene was removed by distillation under reduced pressure. On cooling, almost colorless crystals of the methoxy compound were deposited. This was recrystallized from xylene. The yield was 8 g. or 89%. The product melts at 209° (uncorr.) and is soluble in benzene, carbon tetrachloride, and acetone, but insoluble in water. It is decomposed by 10% sodium hydroxide.

*Analyses.* Subs., 0.2092, 0.2102: 24.54, 24.99 cc. of 0.0521 *N* iodine sol. Calc. for  $C_{17}H_{14}ONAs$ : As, 23.22. Found: 22.92, 23.23.

**7-Ethoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin**,  $HN \begin{array}{c} \diagup C_{10}H_6 \\ \diagdown C_6H_4 \end{array} AS - OC_2H_5$ .—This

compound was prepared in a similar manner, using sodium ethylate. The yield was 76%. The compound melts at 165° (uncorr.) and when recrystallized from absolute ethyl alcohol gives colorless crystals which turn slightly yellow on standing. It is soluble in the common organic solvents and is decomposed by a 10% sodium hydroxide solution.

*Analyses.* Subs., 0.2005, 0.1998: 22.60, 22.49 cc. of 0.0521 *N* iodine sol. Calc. for  $C_{18}H_{16}ONAs$ : As, 22.25. Found: 22.02, 21.99.

**7-*n*-Propoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin**,  $HN \begin{array}{c} \diagup C_{10}H_6 \\ \diagdown C_6H_4 \end{array} AS - OC_3H_7$ .—This

compound was obtained by treating 9 g. of 7-chloro-7,12-dihydro- $\gamma$ -benzophenarsazin with an excess of sodium *n*-propylate. A yield of 7.3 g. (74%) of pale yellow crystals resulted. The compound melts at 152° (uncorr.), is soluble in benzene, acetone and carbon tetrachloride, and is attacked by hot alkalis.

*Analyses.* Subs., 0.2023, 0.1970: 22.28, 21.52 cc. of 0.0521 *N* iodine sol. Calc. for  $C_{19}H_{18}ONAs$ : As, 21.36. Found: 21.52, 21.34.

**7-*n*-Butoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin**,  $HN \begin{array}{c} \diagup C_{10}H_6 \\ \diagdown C_6H_4 \end{array} AS - OC_4H_9$ .—This

compound was obtained by the action of an excess of sodium *n*-butylate on 9 g. of 7-chloro-7,12-dihydro- $\gamma$ -benzophenarsazin dissolved in 200 cc. of xylene. The yield was 6.7 g., or 67%. The almost colorless product is soluble in benzene, acetone and glacial acetic acid. It is decomposed by 10% sodium hydroxide solution. The compound softens slightly at 120° but does not melt completely even at 260°. The same results were obtained with samples prepared from crude *n*-butyl alcohol and the *c. p.* alcohol.

*Analyses.* Subs., 0.1997, 0.2002: 20.95, 20.93 cc. of 0.0521 *N* iodine sol. Calc. for  $C_{20}H_{20}ONAs$ : As, 20.54. Found: 20.49, 20.42.

**7-Phenoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin**,  $HN \begin{array}{c} \diagup C_{10}H_6 \\ \diagdown C_6H_4 \end{array} AS - OC_6H_5$ .—So-

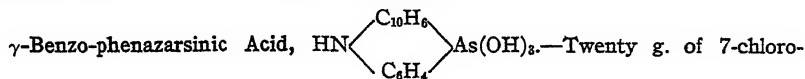
dium phenolate was prepared by dissolving 1.4 g. of metallic sodium in a solution of 8 g. of phenol in 30 cc. of absolute ethyl ether. This was added to 9 g. of 7-chloro-7,12-dihydro- $\gamma$ -benzo-phenarsazin in 200 cc. of xylene, and the usual procedure followed. The compound was deposited in fine yellow needles. The yield was 6.5 g. or 61%. The product melts at 179° (uncorr.), is soluble in the common organic solvents, and readily attacked by a 10% solution of sodium hydroxide.

*Analyses.* Subs., 0.1973, 0.2021: 19.50, 20.03 cc. of 0.0521 *N* iodine sol. Calc. for  $C_{22}H_{16}ONAs$ : As, 19.48. Found: 19.31, 19.36.



By following the above procedure the compound was prepared by adding an excess of sodium benzoate to 9 g. of 7-chloro-7,12-dihydro- $\gamma$ -benzophenarsazin in xylene solution. A yield of 7.3 g., or 67% was obtained. The almost colorless compound melts at 154° (uncorr.). It is soluble in benzene, glacial acetic acid and carbon tetrachloride.

*Analyses.* Subs., 0.2042, 0.2119: 19.55, 20.32 cc. of 0.0521 *N* iodine sol. Calc. for  $\text{C}_{23}\text{H}_{18}\text{ONAs}$ : As, 18.72. Found: 18.70, 18.74.



7,12-dihydro- $\gamma$ -benzo-phenarsazin was dissolved in 800 cc. of glacial acetic acid. To this solution 100 g. of a 3% solution of hydrogen peroxide was added and the whole heated under a reflux condenser for 15 minutes. When the solution had cooled, the acid crystallized in almost colorless needles. The crude product was recrystallized from glacial acetic acid. The yield was 17 g., or 81% of the calculated amount.

The acid does not melt below 260°. It is insoluble in all the common organic solvents, with the exception of glacial acetic acid, and soluble in alkalis in the cold.

*Analyses.* Subs. (dried at 120° for 10 hrs.), 0.2117, 0.1986: 23.40, 22.11 cc. of 0.0521 *N* iodine sol. Calc. for  $\text{C}_{16}\text{H}_{14}\text{O}_3\text{NAs}$ : As, 21.86. Found: 21.59, 21.79.

When the acid is heated to constant weight at 150° it loses one molecule of water giving a form of the arsenic acid containing the more usual grouping  $>\text{As}(\text{O})\text{OH}$ .

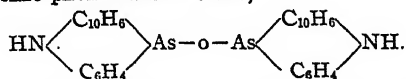
*Analyses.* Subs. (heated to const. wt. at 150°), 0.2312, 0.2146: 31.72, 29.35 cc. of 0.0445 *N* iodine sol. Calc. for  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{NAs}$ : As, 23.07. Found: 22.90, 22.83. Loss on heating at 150°. Subs., 0.4218, 0.4059: wt. lost, 0.0215, 0.0209. Calc. for 1  $\text{H}_2\text{O}$ : 5.24. Found: 5.09, 5.13.

The sodium salt of  $\gamma$ -benzo-phenazarsinic acid was prepared in the following manner. Five g. of  $\gamma$ -benzo-phenazarsinic acid was dissolved in a solution of 0.1 *N* sodium hydroxide. The solution was filtered and concentrated to a small volume on the steam-bath. Upon cooling, the sodium salt was deposited in needle-like crystals, pink in color. After several recrystallizations from 95% alcohol an almost colorless product was obtained. The yield was 5.2 g., or 85%. The sodium salt does not melt below 260°. It is soluble in water (5%), in alcohol and acetone and is quite hygroscopic. It is insoluble in benzene and xylene.

*Analyses.* Subs., 0.2013, 0.2209: 18.40, 19.95 cc. of 0.0521 *N* iodine sol. Calc. for  $\text{C}_{16}\text{H}_{11}\text{O}_2\text{NAsNa}\cdot 4\text{H}_2\text{O}$ : As, 17.89. Found: 17.86, 17.65.

Subs., 0.4527, 0.4853: wt. lost at 150°, 0.0769, 0.0818. Calc. for  $4\text{H}_2\text{O}$ : 17.18. Found: 16.99, 16.86.

7,12-Dihydro- $\gamma$ -benzo-phenarsazin-7-oxide,



—Five g. of 7-chloro-7,12-dihydro- $\gamma$ -benzo-phenarsazin was dissolved in 100 cc. of xylene, and to this was added a solution of 2 g. of freshly prepared silver oxide in 50 cc. of ammonium hydroxide. The slightly yellow oxide precipitated immediately. After heating under a reflux condenser for a few minutes the oxide was filtered hot and washed free from silver with ammonium hydroxide. The yield was 4 g., or 90%. The oxide does not darken or melt below 250°, is soluble in glacial acetic acid and insoluble in benzene, xylene, and carbon tetrachloride.

*Analyses.* Subs., 0.2011, 0.2005: 25.61, 25.49 cc. of 0.0521 *N* iodine sol. Calc. for  $C_{22}H_{22}ON_2As_2$ : As, 25.00. Found: 24.88, 24.84.

7-Bromo-7,12-dihydro- $\gamma$ -benzo-phenarsazin,  $HN \begin{array}{c} \diagup C_{10}H_8 \\ \diagdown C_6H_4 \end{array} As-Br$ .—Five g. of

7-phenoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin was heated under a reflux condenser for 4 hours with an excess of conc. hydrobromic acid. The green, crude product was recrystallized several times from xylene, yielding dark yellow needles. The yield was 3.6 g. or 75%. The crystals melt at 227° (uncorr.). The compound is soluble in benzene, toluene, xylene and glacial acetic acid. It is insoluble in water and is not acted upon by dilute alkalis.

*Analyses.* Subs., 0.1999, 0.1991: 20.41, 20.46 cc. of 0.0521 *N* iodine sol. Calc. for  $C_{16}H_{11}NBrAs$ : As, 20.16. Found: 19.95, 20.08.

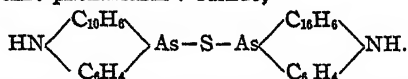
7-Iodo-7,12-dihydro- $\gamma$ -benzo-phenarsazin,  $HN \begin{array}{c} \diagup C_{10}H_8 \\ \diagdown C_6H_4 \end{array} As-I$ .—Three g. of

7,12-dihydro-7-phenoxy- $\gamma$ -benzo-phenarsazin was refluxed for 4 hours with a solution of hydriodic acid made by adding 10 g. of conc. hydriodic acid to 90 cc. of distilled water. The crude product was dark red in color. Upon recrystallization from xylene, beautiful red needles were obtained. The yield was 2.5 g. or 62%. This compound was also prepared in the above manner by heating 7,12-dihydro- $\gamma$ -benzo-phenarsazin-7-oxide with hydriodic acid. The compound melts at 205° (uncorr.), is soluble in benzene, xylene, toluene and glacial acetic acid.

*Analyses.* Subs., 0.2043, 0.1953: 22.15, 21.35 cc. of 0.0445 *N* iodine sol. Calc. for  $C_{16}H_{11}NIAs$ : As, 17.90. Found: 18.10, 18.24.

Subs., 0.1954, 0.2123: AgI, 0.1082, 0.1183. g. Calc. for  $C_{16}H_{11}NIAs$ : I, 30.21. Found: 29.96, 30.14.

7,12-Dihydro- $\gamma$ -benzo-phenarsazin-7-sulfide,



—Three g. of 7-chloro-7,12-dihydro- $\gamma$ -benzo-phenarsazin was dissolved in 500 cc. of absolute ethyl alcohol and hydrogen sulfide bubbled through the solution. A yellow precipitate was formed immediately. As it was insoluble in all common organic solvents the impurities were removed by refluxing with xylene. The yield was 2 g., or 71%. The compound melts at 204–5° (uncorr.).

*Analyses.* Subs., 0.1980, 0.2001: 25.61 26.03 cc. of 0.0497 *N* iodine sol. Calc. for  $C_{22}H_{22}N_2As_2S$ : As, 24.35. Found: 24.12. 24.26.

### Condensation of Diphenylhydrazine and Arsenic Trichloride.

Ten g. of diphenylhydrazine was treated with 12 g. of arsenic trichloride which had been cooled to 5°, and the mixture gently warmed under a reflux condenser. At 34° the reaction became violent and the temperature rose at once to 105°. The mixture began to boil at 130–135° and in the course of 2 hours the boiling temperature rose to 210°, when yellowish vapors appeared in the flask. Upon cooling the reaction mixture solidified to a black granular mass. Recrystallization from xylene gave 8.5 g. of greenish-yellow crystals. Upon recrystallization from carbon tetrachloride fine yellow needles, melting at 192° (uncorr.), were obtained. The compound has the properties and composition of 6-chloro-phenarsazin.

The formation of this compound may be explained by the fact that diphenylhydrazine, at its boiling point, decomposes in part to form diphenylamine and other products.<sup>8</sup> Part of the arsenic chloride, in all probability, acts as a reducing agent and hastens the reaction at a lower temperature. The diphenylamine thus formed then condenses with arsenic trichloride to form 6-chloro-phenarsazin.

Subs., 0.2030, 0.2200: 30.80, 33.30 cc. of 0.0479 *N* iodine sol. Calc. for  $C_{12}H_9NAsCl$ : As, 27.02. Found: 27.29, 27.23.

Subs., 0.4053, 0.4207: 13.98, 13.94 cc. of 0.1 *N* HCl. Calc. for  $C_{12}H_9NAsCl$ : *N*, 5.04. Found: 4.83, 4.85.

### Summary.

1. A brief summary of the chemistry of the nuclear heterocyclic arsenic compounds is presented.

2. The condensation of phenyl- $\alpha$ -naphthylamine with arsenic chloride, and the properties of the resulting 7-chloro-7,12-dihydro- $\gamma$ -benzo-phenarsazin are described.

3. The methods of preparation and the properties of the following derivatives of 7-chloro-7,12-dihydro- $\gamma$ -benzo-phenarsazin are given: 7-methoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin; 7-ethoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin; 7-*n*-propoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin; 7-*n*-butoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin; 7-phenoxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin; 7-benzyloxy-7,12-dihydro- $\gamma$ -benzo-phenarsazin;  $\gamma$ -benzo-phenaz-arsinic acid; 7,12-dihydro- $\gamma$ -benzo-phenarsazin-7-oxide; 7-bromo-7,12-dihydro- $\gamma$ -benzo-phenarsazin; and 7,12-dihydro- $\gamma$ -benzo-phenarsazin-7-sulfide.

EVANSTON, ILLINOIS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]  
 **$\beta,\beta'$ -DICHLORO-DIETHYL ETHER. THE OXYGEN ANALOG OF  
MUSTARD GAS.<sup>1</sup>**

BY OLIVER KAMM AND JOHN H. WALDO.

Received June 27, 1921.

The simple analog of mustard gas in which the sulfur atom has been replaced by oxygen apparently has not been described in the literature. We were therefore interested in studying this compound, not merely in order to compare its physiological action with that of its deadly relative, but also with a view aiming at the possible use of the compound as a new reagent in organic synthesis, particularly in the preparation of cyclic derivatives containing the polymethylene oxide structure.

<sup>8</sup> Stahel, *Ann.*, 258, 244 (1890).

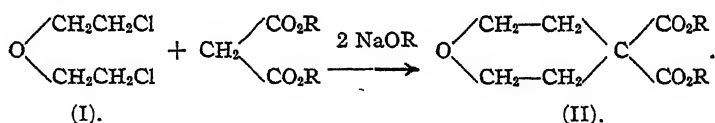
<sup>1</sup> Presented at the St. Louis Meeting of the American Chemical Society, March 1920.

It is not feasible to prepare  $\beta,\beta'$ -dichloro-diethyl ether by the chlorination of ethyl ether for the reason that such a reaction leads to the production of mixtures containing mainly *alpha* chlorination products; it may be prepared conveniently, however, by the general method for the preparation of ethers, *viz.*, by the dehydration of two molecules of the corresponding chloro alcohol. Since the sulfur analog can be prepared readily by the action of sulfur chloride upon ethylene, there is suggested also the possibility of obtaining the oxygen derivative by an analogous reaction:

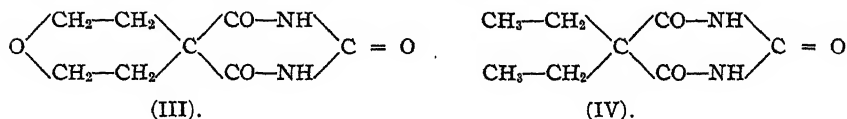


We are indebted to Dr. W. J. Hale, of the Dow Chemical Company for the information that a reaction similar to that expressed by the above equation actually takes place during the manufacture of ethylene chlorohydrin, and that a product identical in physical properties with the ether now characterized by us may be isolated from crude ethylene chlorohydrin.

In addition to the usual analysis, the dichloro-ether has been identified by its condensation with aniline, a reaction which yields an oxazine of known structure, 4-phenyl-morpholin. Because this derivative is a solid, it is well suited for identification purposes. By a slight modification of the usual tautomeric ester synthesis, the dichloro-ether (I) has been condensed with malonic ester to yield 4,4-dicarboxy-ethyl-pentamethylene oxide (II).



This malonic ester derivative should condense readily with urea to yield a new *spiro* derivative of an unusual type, one ring consisting of a pyrimidine and the other of a cyclic oxide structure. This condensation occurs readily. The resultant barbituric acid derivative (III) is closely related in structure to the well-known hypnotic, barbital (IV).



It will be noted that the new compound differs from barbital (veronal) only in the fact that an oxygen atom may be considered as having replaced one hydrogen atom from each of the two methyl groups. The observations made in respect to the difference in physiological action between these two barbituric acid derivatives ultimately should prove of aid in the interpretation of the underlying principles concerning the action of such drugs in the animal body.



### Experimental Part.

**$\beta,\beta'$ -Dichloro-diethyl Ether.**—This compound was prepared by the action of conc. sulfuric acid upon ethylene chlorohydrin. When, by direct analogy, the usual continuous method for the preparation of ethyl ether, was employed, a very poor, almost negligible, yield was obtained. When the alcohol was refluxed with  $\frac{1}{5}$  its weight of conc. sulfuric acid, followed subsequently by direct distillation, the yield was 10% to 15% of the desired product. A further modification of the method consisted in the gradual removal of water during the period of refluxing, this resulted in a yield of about 20% to 25%. Based upon the amount of chlorohydrin actually lost in the process, the yield amounted to about 75%.

A mixture of 200 g. of ethylene chlorohydrin and 35 g. of conc. sulfuric acid was placed in a round-bottom boiling flask and heated under a reflux condenser for 6 hours. During this refluxing period, the water in the condenser was maintained at 90° to 100° and the heating regulated so that a very slow but continuous removal of water and chlorohydrin was effected. This distillate consisted mainly of the constant-boiling mixture of the alcohol and water,<sup>2</sup> and was saved, together with the subsequent distillate, for recovery of chlorohydrin. About  $\frac{1}{2}$  the volume of the reaction mixture was removed during the refluxing period, after which the liquid was distilled directly through a horizontal condenser. This distillation, in spite of the formation of sulfur dioxide, was continued until only a charred mass remained in the fractionating flask. The distillate was washed with sodium carbonate solution, dried with sodium sulfate, and then subjected to careful fractionation, with the aid of an efficient column.

The  $\beta,\beta'$ -dichloro-diethyl ether is a colorless oil with a pleasant ethereal odor; b. p., 177–8° (corr.);  $d_{20}^{20}$ , 1.213;  $n_{20}^{20}$ , 1.457.

**Analysis.** Subs., 0.2417, 0.1910: 33.24 cc., 26.27 cc. of 0.1 *N* AgNO<sub>3</sub>. Calc. for C<sub>4</sub>H<sub>8</sub>OCl<sub>2</sub>: Cl, 49.6. Found: 48.8, 48.8.

**4-Phenyl-morpholin.**—A mixture of 72 g. of the dichloro ether and 47 g. of aniline was heated for about 10 hours under a reflux condenser with sufficient 10% aqueous sodium hydroxide to remove the hydrochloric acid liberated in the reaction. The oily reaction product was extracted with ether and the solvent layer washed with several small portions of 1% hydrochloric acid in order to remove those impurities more basic than the desired oxazine. Upon evaporation of the ether, an oily mass of crystals remained, from which the residual oil was removed by pressing the crystals on a porous clay plate. The remaining solid was then crystallized from 50% aqueous alcohol and obtained in the form of almost white flakes melting at 57° to 58°. Upon distillation, a pure white product was obtained boiling at 259° to 260°, at 745 mm. These constants, together with the chlorine analyses recorded above, establish the constitution of the dichloro-diethyl ether.

**4,4-Dicarboxyethyl-tetrahydro-pyran.**—One-half mole of sodium was dissolved in 200 cc. of absolute ethyl alcohol. To the sodium ethylate solution,  $\frac{1}{2}$  mole of malonic ester and 72 g. ( $\frac{1}{2}$  mole) of the dichloro-diethyl ether were added, and the mixture was refluxed on the water-bath for an hour. The flask containing the reaction mixture was then cooled, an alcoholic solution of a second  $\frac{1}{2}$  mole of sodium ethylate added, and the mixture was refluxed again during an hour. After cooling the reaction mixture, the sodium chloride was separated by filtration, the major portion of the alcohol removed by distillation, and the remaining product treated with water. The oil which separated was extracted with ether. The ether solution was dried over anhydrous sodium sulfate and subjected to distillation with the use of a short but fairly efficient fractionating column. Yield 30 g. (26%).

<sup>2</sup> THIS JOURNAL, 41, 1422 (1919).

The 4,4-dicarboxyethyl-tetrahydro-pyran is a liquid boiling at  $260^{\circ}$  (740–745 mm.);  $d_{20}^{20}$ , 1.107. It was not subjected to analysis, but its condensation product with urea served for its analytical identification. Its physical and chemical properties agree with the assigned formula (II).

In one experiment, the above directions were modified and the total quantity of sodium ethylate was used at one time. This variation resulted in the formation of an appreciable quantity of a higher-boiling product consisting partly, no doubt, of the ethoxy derivative,  $C_2H_5-O-CH_2-CH_2-O-CH_2-CH_2-CH < (C(O)OC_2H_5)_2$ .

**Tetrahydro-pyran-4,5-spiro-2,4,6-triketo-hexahydro-pyrimidine.**<sup>3</sup>—This barbituric acid derivative was prepared by the well-known condensation of malonic ester derivatives with urea in the presence of sodium ethylate.

A 2.5 g. portion of sodium was dissolved in 35 cc. of absolute ethyl alcohol. This sodium ethylate solution, together with 10 g. of 4,4-dicarboxyethyl-tetrahydro-pyran and 3.3 g. of finely powdered urea, was heated in a sealed tube for 5 hours at  $100^{\circ}$  to  $105^{\circ}$ . The reaction mixture was then filtered, the mass of sodium salts treated with dil. hydrochloric acid, and the insoluble barbituric acid derivative separated by filtration. The product was purified by crystallization from hot water. Yield, 41%.

This barbituric acid derivative is a white crystalline product melting at  $218^{\circ}$ . It crystallizes with one molecule of water which, however, is gradually lost if it is dried at  $110^{\circ}$ , as may be seen from the following data.

Subs., 0.6170: heated at  $110^{\circ}$ . Calc. loss, 0.0510; Found: 0.0514. Loss in weight with time: 1st. hour, 0.0302; 2nd. hour, 0.0206; 3rd. hour, 0.0004; 4th. hour, 0.0002.

*Analysis.* Subs., 0.2034:  $N_2$ , 25.40 cc. (727.5 mm. and  $29^{\circ}$ ).

Subs., 0.2336:  $H_2O$ , 0.1148;  $CO_2$ , 0.3767. Calc. for  $C_8H_{10}O_4N_2 \cdot H_2O$ : C, 44.4; H, 5.60; N, 12.96. Found: C, 43.9; H, 5.49; N, 12.9.

### Physiological Behavior of $\beta, \beta'$ -Dichloro-diethyl Ether and of Tetrahydro-pyran-4,5-spiro-2,4,6-triketo-hexahydro-pyrimidine.

The explanation appears to be generally accepted that  $\beta, \beta'$ -dichloro-diethyl sulfide exerts its highly toxic influence upon the tissues because of the liberation of hydrochloric acid within the body cells. The physical properties of the compound are apparently such as to yield exactly the requisite relationship between the rate of penetration of the compound and its rate of hydrolysis to produce the well-known toxic effect. It was therefore of interest to test the corresponding oxygen ether for the possibility of a related effect; it was found, however, that  $\beta, \beta'$ -dichloro-diethyl ether exerted no similar deleterious action upon the tissues; in fact, liberal quantities of the ether were applied directly to the skin without a noticeable effect.

The close structural relationship between the well-known hypnotic, barbital, and the new barbituric acid derivative, tetrahydro-pyran-4,5 *spiro*-2,4,6-triketo-hexahydro-pyrimidine, has been briefly referred to above. The *spiro* compound was found to possess no hypnotic and no toxic effect when administered orally to a rabbit of about 1.5 kg. weight in

<sup>3</sup> This system of nomenclature has been proposed recently by Dox and Yoder, *THIS JOURNAL*, 43, 678 (1921). The numerals preceding the word *spiro* mean that the *spiro* carbon corresponds to Position 4 in the pyran ring and Position 5 in the pyrimidine ring.

lg. doses. Barbitol, on the other hand, is effective<sup>4</sup> even in considerably smaller amounts, the fatal dose for rabbits being about 0.35 g. per kg. body weight.

The above difference in physiological effect is unusual for the reason that di-alkyl derivatives of barbituric acid are practically all effective unless, of course, the alkyl groups are sufficiently high in molecular weight, as in the dibenzyl compound, to produce compounds of limited solubility. The new derivative, in which we may consider that the two alkyl groups have been united through an oxygen atom, does not differ greatly from barbitol in its physical properties; therefore one must seek elsewhere an explanation for its lack of activity.

The observation that the new derivative is in combination with water to form a monohydrate suggests one possible explanation for its non-activity, particularly so, since barbitol does not crystallize as a hydrate under similar experimental conditions. We are inclined, however, to a different explanation.

It is known that when barbitol is administered to an animal a considerable percentage of the drug is eliminated unchanged. The *spiro* derivative appeared, however, in the urine in the form of fine needles melting in the neighborhood of 150° to 160°. Unfortunately, because of the limited physiological study, we neglected to seek an identification of the transformation product as eliminated from the animal body. There is a possibility that in this instance, because of the *spiro* structure, the compound is more susceptible to hydrolysis *in vivo*. Whether or not this view is correct may be determined when reports are available concerning the physiological behavior of related cyclic derivatives.

### Summary.

1.  $\beta,\beta'$ -Dichloro-diethyl ether has been prepared by the dehydration of ethylene chlorohydrin.

2. The new dichloro ether was condensed with malonic ester and yielded 4,4-dicarboxyethyl-tetrahydro-pyran. This di-substituted malonic ester derivative was condensed with carbamide and yielded a substituted barbituric acid of the *spiro* type.

3.  $\beta,\beta'$ -Dichloro-diethyl ether possesses no baneful effect upon the tissues of the animal body, an action which is so striking in the case of the sulfur analog known as *mustard gas*.

4. Tetrahydro-pyran 4,5-*spiro*-2,4,6-triketo-hexahydro-pyrimidine, although closely related in structure to barbitol, possesses no marked hypnotic properties. In contrast to the latter compound, it is modified within the animal body. The ready formation of an inert hydrolytic product probably accounts for its physiological behavior.

URBANA, ILLINOIS.

<sup>4</sup> *Biochem. Z.*, 31, 1 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

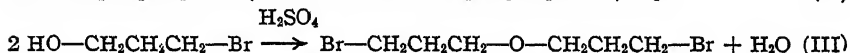
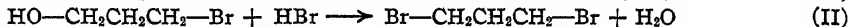
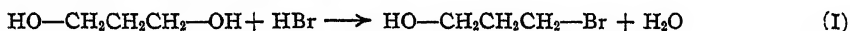
 $\gamma, \gamma'$ -DIHALOGENO-DIPROPYL ETHERS.

BY OLIVER KAMM AND WALTER H. NEWCOMB.

Received June 27, 1921.

The present work was undertaken in order to prepare the symmetrical  $\gamma$ -dichloro and dibromo substitution products of dipropyl ether, compounds which may prove of value in the synthesis of certain heterocyclic derivatives containing rings of more than 6 atoms. By analogy to the preparation of  $\beta, \beta'$ -dichloro-diethyl ether described in the preceding paper, the derivatives of dipropyl ether were prepared by subjecting trimethylene-chloro- and bromohydrins to dehydration.

Trimethylene bromide is readily prepared from the corresponding glycol, even with aqueous hydrobromic acid. The presence of sulfuric acid increases the yield.<sup>1</sup> Accordingly an attempt was made to prepare the bromohydrin by an analogous reaction. Since trimethylene glycol is practically non-volatile with water vapor while the bromohydrin is appreciably volatile, the latter compound may be continuously removed from the reaction mixture, a procedure which should tend to favor Reaction I at the expense of Reaction II.



Unfortunately, the reaction velocity of the step illustrated by Equation II is far greater than that of Step I, and consequently in spite of the use of a considerable excess of trimethylene glycol, the dibromide represents the largest percentage of the yield. Simultaneously with the formation of the first two products a third reaction takes place as represented by Equation III. The desired dibromo ether may therefore be isolated during the preparation of the bromohydrin.

Preliminary experiments have been conducted in the endeavor to convert  $\gamma, \gamma'$ -dibromo-dipropyl ether into hexamethylene oxide by the removal of the bromine atoms by means of metals. These reactions, however, have yielded products contaminated with di-allyl ether and dipropyl ether, together with products which are probably mixed ethers, and we are unable at present to offer a feasible method for the preparation of this unknown cyclic ether.

## Experimental Part.

Trimethylene chlorohydrin was prepared with aqueous hydrochloric acid, in a manner analogous to that described (p. 2229) for the preparation of the bromohydrin. In view of the fact that an improved method has

<sup>1</sup> THIS JOURNAL, 42, 301 (1920).

recently been contributed from the Eastman Laboratory<sup>2</sup> we omit a discussion of our own results.

$\gamma,\gamma'$ -Dichloro-dipropyl ether was obtained in 10–15% yield by refluxing trimethylene chlorohydrin with 20% of its weight of sulfuric acid. The ether is a colorless oil boiling at 215° at 745 mm.,  $d_{20}^{20}$  1.140.

**Preparation of Trimethylene Bromohydrin and of  $\gamma,\gamma'$ -Dibromo-dipropyl Ether.**

To 3 moles of trimethylene glycol in a 1-liter distilling flask add 1 mole of sulfuric acid and  $1\frac{1}{2}$  moles of hydrobromic acid in the form of the aqueous 48% solution. This mixture is distilled until the distillate is equal in volume to the hydrobromic acid solution added. 1 mole of the glycol and 1 mole of hydrobromic acid are added and the distillation repeated until the volume of the distillate is again equal to the volume of the hydrobromic acid solution added. The molar additions of hydrobromic acid and of the glycol and the distillations may be repeated as many times as may be desired. The halogen derivatives of the glycol distil over with water and the distillate separates into two layers. At the end of the distillation, which is finally carried to the stage at which considerable charring takes place, the distillate is neutralized with sodium carbonate and the two layers separated. The oily layer containing the organic derivatives is dried over anhydrous sodium sulfate. The aqueous layer is extracted with ether in order to remove any of the bromohydrin which is dissolved therein, and the ether extract is also dried with anhydrous sodium sulfate. The ether is distilled leaving the nearly pure bromohydrin which is subjected to fractional distillation. The main product is distilled until a temperature of 170° is reached, in order to remove most of the trimethylene bromide, and the remaining residue is distilled under diminished pressure. By means of a careful refractionation with the use of a column, a separation of the trimethylene bromide from the trimethylene bromohydrin may be attained.

The separation of the bromohydrin from the dibromo-dipropyl ether which is also formed in the reaction can be easily accomplished because of the wide difference between the boiling points of the two products. The yield of the derivatives depends somewhat on the number of additions of glycol and hydrobromic acid. The increase in the number of additions decreases the yield of the dibromide and increases the yield of the bromohydrin and of the dibromoether. A limit to the number of additions, however, is reached because of the charring of the reaction mixture.

The following table gives the average yields of several runs by the above process. The percentage yields are calculated on the possible theoretical yield for each substance based upon the amount of hydrobromic acid used. 85 to 95% of this amount is accounted for in the combined yields.

No. of extra additions of HBr and glycol.	Glycol used G.	HBr used G.	Yield of dibromide.	Yield of bromohydrin.	Grams of dibromo ether.
2	380	283.5	214 g. 60%	86 g. 17%	48 g. 10.7%
5	608	526.5	372.5 g. 57%	210.5 g. 23%	126.7 g. 15%

The dibromo-dipropyl ether is a colorless liquid which undergoes slight decomposition when distilled under ordinary pressure. It boils at 128° at 19 mm.;  $d_{20}^{20}$  1.574. As might be expected from its structure, this ether is insoluble in water, but is soluble in the common organic solvents; it is also appreciably volatile with water vapor. In solubility and volatility, dichloro-ethers derived from ethylene- and trimethylene chlorohydrins, show a close resemblance to dibromo-dipropyl ether.

<sup>2</sup> THIS JOURNAL, 43, 369 (1921).

*Analysis.* Subs., 0.2030, 0.1716; AgBr, 0.2902, 0.2456. Calc. for  $C_6H_{12}OBr_2$ : Br, 61.5. Found: 60.8. 60.9.

### Summary.

$\gamma, \gamma'$ -Dichloro- and dibromo-dipropyl ethers have been prepared and their physical properties recorded.

URBANA, ILL.

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[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY.]

## THE ACTION OF AMMONIA WATER ON DICYANDIAMIDE.<sup>1</sup>

BY TENNEY L. DAVIS.

Received July 1, 1921.

Dicyandiamide hydrolyzed with sulfuric acid produces one molecule of guanidine sulfate and one of ammonium sulfate, and guanidine sulfate may be obtained in satisfactory yields by this process.<sup>2</sup> But dicyandiamide is most readily prepared from Lime-nitrogen, from which ammonia may be produced more readily by simpler methods—and the production of ammonia from dicyandiamide in a process where guanidine is the object might well be regarded as the virtual loss of one quarter of the nitrogen which has earlier been "fixed" in the form of Lime-nitrogen and of dicyandiamide. We<sup>1</sup> have studied the reaction of ammonia on dicyandiamide with the expectation that it would lead to the formation of guanidine or of guanidine carbonate without the agency of mineral acid, and in the hope that it might perhaps lead to the formation of two molecules of guanidine from one of dicyandiamide.

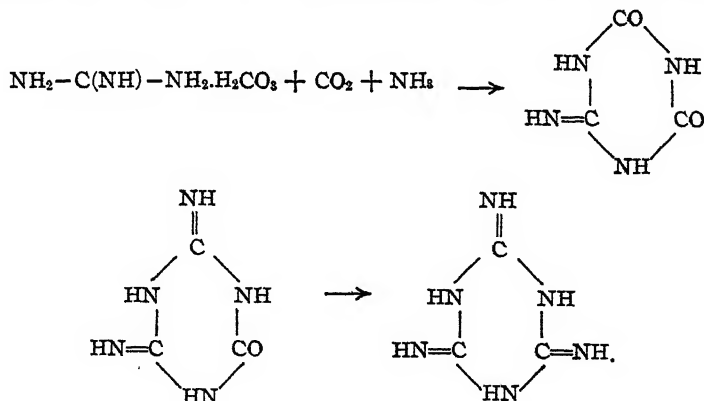
We find that the action of ammonia water on dicyandiamide when the materials are heated together in a sealed tube is simple hydrolysis, water only being effectively involved and the dicyandiamide being converted first into guanylurea and later into guanidine carbonate. We have followed the progress of the reaction by precipitating the solution with ammonium picrate and have been able to judge from the melting point whether the precipitate consisted of picrate of guanidine or of picrate of guanylurea. After relatively short durations of heating at 150°, guanylurea was found in the product and the reaction mixture contained no appreciable amount of insoluble material. When the reaction was of longer duration or at a higher temperature, guanidine was formed and the reaction mixture contained considerable quantities of ammeline and ammelide. When the reaction was carried on for a still longer time, no guanidine was found and

<sup>1</sup> This investigation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. In this work I have been assisted by William S. Johnson. T. L. D.

<sup>2</sup> THIS JOURNAL, 43, 669 (1921).

a large quantity of melamine was isolated along with the ammeline and ammeline.

Bamberger<sup>3</sup> reports that dicyandiamide heated with water at 160–170° yields carbon dioxide, ammonia and ammeline. He reports also the formation of ammeline by heating dicyandiamide with ammonium carbonate at 120°. Either reaction would account for the formation of ammeline under the conditions of our experiments. The formation of melamine in our experiments and the disappearance of the guanidine carbonate which is first formed would seem to indicate that the melamine is produced from the guanidine salt. Smolka and Friedreich<sup>4</sup> report that guanidine carbonate at 180–190° gives carbon dioxide, ammonia and melamine, and that dicyandiamide and ammonium carbonate at 160° give the same products. We find that guanidine carbonate heated with ammonia water at 160° for 2 hours gives melamine—and believe that the formation of the mono-, di-, and tri-imides of cyanuric acid in our experiments is plausibly explained by supposing that guanidine carbonate reacts with carbon dioxide and ammonia to form first ammeline (the mono-imide), then ammeline (the di-imide), and finally melamine (the tri-imide), as follows.



When Lime-nitrogen is leached with hot water and the solution is evaporated, dicyandiamide is formed, but more or less ammonia is always produced, and the tailings from the crystallization of dicyandiamide are strongly basic, viscous and caustic liquids which deposit insoluble white materials. The foregoing considerations help to explain the genesis of these products.

### Discussion of Experiments.

**Effect of Ammonia Water.**—A systematic series of sealed tube experiments, with 4 g. of dicyandiamide and 7.5 cc. of ammonia water (sp. gr. 0.90) was carried out.

<sup>3</sup> Bamberger, *Ber.*, 16, 1074, 1703 (1883).

<sup>4</sup> Smolka and Friedreich, *Monatsh.*, 10, 91, 93 (1889).

After the heating, the contents of the tubes were rinsed out, filtered, and precipitated by the addition of ammonium picrate solution. The precipitated picrate was washed and dried, and its melting point was determined. Guanylurea picrate turns deep red at 235° and at 265° it turns black and decomposes but does not melt. Guanidine picrate melts with decomposition at 310–320°. The results were as follows:

Temperature. ° C.	Time. Hours.	Weight of G. picrate.	Melting point. ° C.
100	2	0	—
	4	0	—
	6	0	—
	8	0	—
	1	0	—
	2	trace	—
150	3	0.4	265 decomp.
	4	1.1	
	5	1.6	
	6	1.4	
	7	0.9	
	8	0.7	
*	9	0.6	310–320
*	0.5	0.8	
*170	1	1.8	
*	1.5	1.8	
180	1	2.2	
*	10 min.	0.4	
	20	— exploded	—
*	1 hour	3.2	310–320
*200	1.5	1.6	
*	2	0.6	
	2.5	— exploded	

In the experiments which are marked with an asterisk (\*) a white insoluble compound was obtained. This was filtered off before precipitating with ammonium picrate, and was later identified as a mixture of ammeline and ammeline. Since the yields of guanidine were poor, it was judged that too much ammonia water had perhaps been used, so making the reaction mixture too dilute in dicyandiamide, and another series of experiments was carried out to test this point. Four g. of dicyandiamide was used in each experiment.

Volume of ammonia water (0.90). Cc.	Time. Hours.	Temperature. ° C.	Weight of G. picrate.	Melting point. ° C.
*3	1	160	3.5	310–320
*4			3.4	
*5			4.1	
*4		170	2.5	
*4		180	2.4	
5	2	150	1.1	265
5			— exploded	—
5			3.9	265



Since the best yield was obtained by heating 4 g. of dicyandiamide with 5 cc. of ammonia water at  $160^{\circ}$  for 1 hour, an experiment with the materials in the same relative proportion was tried on a larger scale. Fifty g. of dicyandiamide and 62.5 cc. of ammonia water (0.90) were heated in an autoclave at  $160^{\circ}$  for 1 hour, but the autoclave was heavy and required several hours to cool before it could be opened, and the high temperature was actually maintained for much more than 1 hour. The reaction mixture contained no guanidine; it yielded a considerable quantity of the familiar insoluble white material, together with 13.2 g. of a substance which crystallizes from water in white glistening leaflets or in thick rhomb-shaped plates, which does not melt below  $360^{\circ}$ , and which has been identified as melamine by its properties and by analysis.

**Guanidine Carbonate and Ammonia Water.**—To test the hypothesis that the melamine was produced by the secondary reaction of ammonia on the guanidine carbonate first formed 1.5 g. of guanidine carbonate (from the thiocyanate) and 5 cc. of 6 *N* ammonia water were heated together in a sealed tube at  $160^{\circ}$  for 6 hours. The reaction mixture yielded about 1 g. of melamine, identified by its reactions and properties. It contained not more than traces of ammeline and ammelide.

**Action of Sodium Carbonate.**—To confirm the idea that the conversion of dicyandiamide to guanidine by the action of ammonia water might be due to the action of hydroxyl ions rather than to that of the ammonia itself, a tube containing 2 g. of dicyandiamide and 6.5 cc. of 3 *N* sodium carbonate solution was heated for 1 hour at  $160^{\circ}$ . The precipitated picrate weighed 1.9 g. and melted with decomposition at  $310\text{--}320^{\circ}$ .

### Summary.

Ammonia water acts on dicyandiamide in the same way that other hydrolytic agents do, converting it first into guanylurea and later into guanidine carbonate. The guanidine carbonate enters into a secondary reaction with the ammonia, and is converted finally into melamine.

CAMBRIDGE 39, MASSACHUSETTS.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY.]

## PREPARATION OF GUANIDINE NITRATE.<sup>1</sup>

BY TENNEY L. DAVIS.

Received July 1, 1921.

When the paper of Werner and Bell<sup>2</sup> appeared in which the preparation of guanidine thiocyanate is described by the heating together of dicyandiamide and ammonium thiocyanate, it occurred to us that guanidine nitrate might perhaps be prepared similarly by the heating together of dicyandiamide and ammonium nitrate. Experiment quickly confirmed the belief, and the yields were found to be excellent.

Guanidine thiocyanate is deliquescent, difficult to purify, and unpleasant to handle. The nitrate is not deliquescent; it is easy to purify, and offers advantages to the worker who wishes an easily made salt of guanidine. For the explosive industry the nitrate possesses another great advantage, for nitroguanidine prepared from the thiocyanate still contains traces of sulfur compounds and is not fit for use in nitrocellulose powder since it impairs the powder's stability and causes it to blister on storage. Nitroguanidine may be prepared in excellent yield simply by dissolving guanidine nitrate in conc. sulfuric acid and pouring the solution into water. Studies on the preparation of the nitroguanidine by this method and of its reaction with and solubility in sulfuric acid of various concentrations are now practically completed at this laboratory and will form the subject of a later communication.

In a preliminary experiment dicyandiamide and two molecular equivalents of ammonium nitrate were heated together in a test-tube in an oil-bath at 160° until the mass which first fused had become practically solid again at that temperature. The product was found to consist almost entirely of guanidine nitrate. When this result was discussed in March 1921 with the chemists of the Fixed Nitrogen Research Laboratory, it appeared that the paper of Werner and Bell had induced Mr. Blair of that laboratory to try a similar experiment. He had worked at a lower temperature (135°) and had obtained no guanidine but had obtained the nitrate of biguanide. A reaction similar to this had long ago been noted by Smolka and Friedreich<sup>3</sup> who obtained biguanide chloride by heating together dicyandiamide and ammonium chloride in alcoholic solution in a sealed

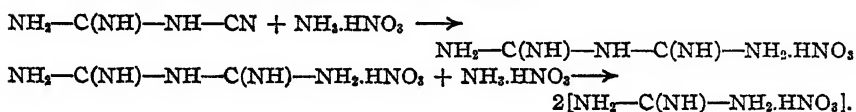
<sup>1</sup> This investigation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. In this work I have been assisted by Edward F. English. T. L. D.

<sup>2</sup> Werner and Bell, *J. Chem. Soc.*, 118, 1133 (1920).

<sup>3</sup> Smolka and Friedreich, *Monatsh.*, 9, 228 (1888).

tube. They found also,<sup>4</sup> as did Bamberger and Dieckmann later,<sup>5</sup> that the same materials yielded biguanide chloride if simply melted together. Rathke,<sup>6</sup> even earlier, had actually obtained guanidine by the reaction; from the heating of dicyandiamide and ammonium chloride in aqueous solution at 150° he obtained ammelide and the chlorides of biguanide and of guanidine. Blair suggested that perhaps one molecule of ammonia added to dicyandiamide to form biguanide and that the biguanide reacted with a second molecule of ammonia to form guanidine. We have verified these suggestions by experiment. Since chance had led us first to prepare guanidine nitrate, the chemists of the Fixed Nitrogen Research Laboratory very kindly agreed, in order to avoid duplication of effort, to experiment no more on the formation of guanidine nitrate by the heating together of ammonium nitrate<sup>7</sup> and dicyandiamide but to devote their attentions to other methods for the preparation of guanidine nitrate from lime-nitrogen for the study of which the peculiar facilities of their laboratory were especially adapted.

The mechanism of the reaction is as follows.



We have demonstrated the truth of these equations by showing (1) that dicyandiamide and two molecules of ammonium nitrate at 120° yield biguanide nitrate, (2) that the same materials at 160° give guanidine nitrate, and (3) that biguanide nitrate and ammonium nitrate in molecular proportions fused together give guanidine nitrate. The reaction therefore is not dependent upon the depolymerization of dicyandiamide as Werner and Bell have supposed.

Since the biguanide nitrate which is first formed by the addition of one molecule of ammonium nitrate to one of dicyandiamide is strongly basic and tends to react with a second molecule of ammonium nitrate to form the normal nitrate and to liberate ammonia, we found it expedient in preparing guanidine nitrate to work with a slight excess, *i. e.*, with 2.2 mols. of ammonium nitrate.

When a small quantity of a mixture of dicyandiamide and ammonium nitrate in molecular proportions is carefully melted in a test-tube, ammonia is given off and the product if cooled promptly contains a large quantity

<sup>4</sup> Smolka and Friedreich, *Monatsh.*, 10, 86 (1889).

<sup>5</sup> Bamberger and Dieckmann, *Ber.*, 25, 545 (1892).

<sup>6</sup> Rathke, *ibid.*, 18, 3107 (1885).

<sup>7</sup> German pat. 222,552 of October 30, 1908, ought to be noted in this connection. It describes the preparation of guanidine salts by the dry heating together of dicyandiamide and ammonium salts *in molecular proportions*. We find that two molecules of the ammonium salt are necessary for the reaction and that the product is two molecules of the guanidine salt.

of nitrate of biguanide. If, however, a larger quantity of the same mixture, say 150 g., is heated in a beaker carefully with a free flame, a violent reaction sets in at the moment that the mass fuses clear, much heat is disengaged, ammonia comes off abundantly, a white substance precipitates in the hot liquid and somewhat more than half of the dicyandiamide is converted into ammeline (along with a little ammelide) while somewhat less than half appears in the form of guanidine nitrate.

A mixture of one mol. of dicyandiamide and two mols. of ammonium nitrate heated at 120° sinters together after a time and assumes a porridge-like consistency. After 6 hours' heating the mass contains considerable unchanged dicyandiamide and ammonium nitrate together with biguanide nitrate and a small quantity of guanidine nitrate. At 130° the same mixture fuses within an hour to a clear colorless liquid which undergoes no apparent change during a further 2 hours of heating, and yields considerable guanidine and biguanide. At 120° in the autoclave with water the same mixture, after 2 hours' heating, yields the same products as when the heating is carried out for a longer time in the absence of water.

A mixture of dicyandiamide and 2.2 mols. of ammonium nitrate heated at 160° fuses to a colorless liquid which soon begins to deposit crystals and becomes practically solid at the end of 2 hours' heating. From the product we have isolated guanidine nitrate in amounts equal to more than 85% of the calculated yield. The same materials heated in an autoclave at 160° for 2 hours with water or with alcohol give practically the same yields of guanidine nitrate, but alcohol appears to be no better than water for the purpose. A temperature higher than 160° appears to offer no advantage.

Experiments with the nitrates of substituted ammonias are now under way in this laboratory.

### Discussion of Experiments.

**Sealed Tube Experiments.**—Five g. of dicyandiamide, 9 g. of ammonium nitrate, and 11 cc. of absolute alcohol were heated together in a sealed tube for 1 hour at 160°. When the tube was opened, a slight odor of ammonia was perceptible and the contents gave off a disagreeable putrid odor similar to that which is produced in the synthesis of malonic ester from chloro-acetic acid. The contents of the tube consisted of white crystalline shiny plates. On recrystallization from moist alcohol these yielded 12 g. of guanidine nitrate, m. p., 212° (pure guanidine nitrate, m. p., 215–216°); calculated yield, 14.5 g.; actual yield, 82.7%. The product was identified as guanidine nitrate by its own melting point, by the melting point of its picrate, and by the fact that it yielded nitroguanidine on treatment with sulfuric acid.

A similar experiment in which 10 cc. of water was used instead of the alcohol yielded 13 g. of guanidine nitrate, m. p., 212°; or 89.6%. We conclude that water is preferable to alcohol.

**Autoclave Experiments.**—For the purpose of determining the best conditions for the reaction, other experiments were carried out in a small autoclave of about 100cc. capacity. After the autoclave had been closed, it was immersed in a bath of heated

oil the temperature of which was determined by means of a thermometer. After the heating, the autoclave was cooled promptly by immersion first in oil and later in cold water. 16.8 g. of dicyandiamide, 33.6 g. of ammonium nitrate, and 20 cc. of water were heated at 130° for 1 hour. The first crude product amounted to 45 g. and gave a test for biguanide nitrate. Recrystallized from alcohol it was found to consist in large part of guanidine nitrate and the first crystal fraction gave no test for biguanide. The mother liquors contained biguanide, and, worked up by recrystallization from alcohol and from water, yielded about 2 g. of biguanide nitrate.

A similar experiment at 160° for 2 hours yielded, after the product was recrystallized from water, 42 g. of guanidine nitrate, m. p., 206°, and 1.2 g. of white insoluble material (ammeline and ammelide). The calculated yield was 48.8 g. of guanidine nitrate, the actual yield, 86.0%. An experiment for a longer time, 3 hours at 160°, gave practically the same result, 42 g. of guanidine nitrate, m. p., 209°, and 1.1 g. of the white insoluble by-product.

A similar experiment at a higher temperature, 180° for 2 hours, gave the same yield of guanidine nitrate, 42 g., m. p. 208–209°, but it yielded considerably more, 4.8 g., of the insoluble white material.

**Fusion Experiments.**—An experiment without any solvent gave results as gratifying as those which were obtained from the autoclave. Five g. of dicyandiamide and 9 g. of ammonium nitrate were mixed in a dry test-tube and heated in the melting-point bath at 160° for 2 hours. The mass first fused to a colorless liquid and ammonia was evolved. It soon began to deposit crystals which increased in amount as the heating was continued, and the material became an almost solid mass at the end of an hour. The heating was continued for another hour in order to drive the reaction to completion. The product was entirely soluble in water and yielded, on recrystallization from this solvent, 13 g. of guanidine nitrate, m. p. 210°; or 89.6%.

An experiment at a lower temperature yielded considerable biguanide. A mixture of 4.2 g. of dicyandiamide and 10 g. of ammonium nitrate was heated at 130° in a dry test-tube in the oil-bath. At the end of half-an-hour the mass had melted (except for a few crystals) to a colorless liquid. No further change appeared when the heating was continued for an hour. The product was readily soluble in water. Half of the resulting solution, treated with ammonium picrate, yielded 2.0 g. of guanidine picrate, m. p. 310–315°. The other half, treated with ammoniacal copper nitrate, yielded 0.6 g. of the characteristic copper-biguanide nitrate. When ammoniacal copper nitrate was added, a flocculent precipitate was produced but its color could not be seen because of the intense blue color of the solution. The precipitate was filtered off on asbestos and rinsed with water. The contents of the filter, asbestos and all, boiled up with water and filtered through paper, yielded a bright purple solution which deposited on cooling rose-colored needles of copper-biguanide nitrate.

A mixture of 84 g. of dicyandiamide and 80 g. of ammonium nitrate was carefully warmed in a Pyrex beaker. The mass started to melt readily enough, but at the moment when it fused clear, even though the flame was withdrawn, a violent reaction set in, ammonia fumes were given off in great abundance, the mass heated up greatly, effervesced, and deposited a white solid. After cooling, the product resembled chalk or porcelain. Worked up with water, it yielded 62 g. of guanidine nitrate, m. p. 209°, 56 g. of ammeline and 6.3 g. of ammelide. The mother liquors gave no test for biguanide with ammoniacal copper nitrate.

Half a gram each of biguanide nitrate and ammonium nitrate were brought to fusion together in a dry test-tube. The product, taken up in water and precipitated with ammonium picrate, yielded guanidine picrate, m. p. 316–320° with decomposition.

### Summary.

Guanidine nitrate may be obtained in excellent yield by heating dicyandiamide for 2 hours at 160° with slightly more than 2 molecules of ammonium nitrate, using either the dry materials alone or the materials and water in an autoclave.

CAMBRIDGE, 39, MASSACHUSETTS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## AN INDIRECT METHOD OF PREPARATION OF ORGANIC MERCURIC DERIVATIVES AND A METHOD OF LINKING CARBON TO CARBON.

### Preliminary Report.<sup>1</sup>

BY MORRIS S. KHARASCH.<sup>2</sup>

Received July 5, 1921.

The study of organic metallic derivatives is of considerable importance not only because of the use they can be put to synthetically, but also of the opportunity they afford to attack, from an entirely different angle, problems of great theoretical moment. The methods at our disposal suitable to the preparation of any type of mercury compound are, however, rather limited. The main difficulty arises from the fact that mercury never orients *meta* to the group already present in the molecule in the case of a mono substituted benzene derivative. Even in such compounds as nitrobenzene and benzoic acid the mercury orients to the *ortho* and not the *meta* position. This is rather significant if taken in conjunction with the fact that in the mercurization of a compound containing an electronegative group the *para* compound is formed in much larger quantity than the *ortho*.

It is, therefore, quite evident that one has to develop indirect methods of preparing mercury derivatives, otherwise the scope of investigation is necessarily limited, especially in the case of compounds containing one or more electropositive groups.

In a recent paper Kharasch and Chalkley<sup>3</sup> have shown that the sulfinic acid method can be used for introducing mercury in any desired position in the benzene molecule, by the use of the corresponding sulfinic acid, the mercury taking the place of the SOOH radical. Unfortunately the preparation of the corresponding sulfinic acids is at times exceedingly difficult, and the writer has, therefore, been led to a search for a simpler and less time consuming method.

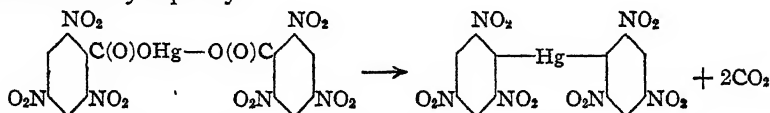
<sup>1</sup> Read before the Organic Division of the American Chemical Society at the Rochester Meeting, March 1921.

<sup>2</sup> National Research Fellow in Organic Chemistry.

<sup>3</sup> Kharasch and Chalkley, *THIS JOURNAL*, 43, 607 (1921).

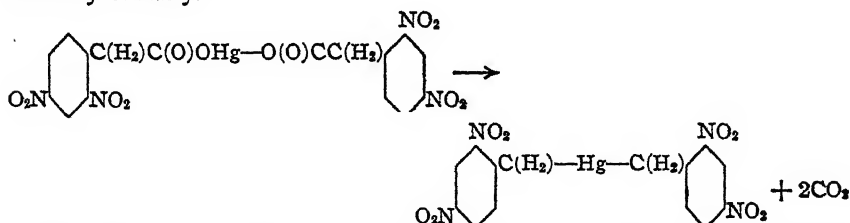
The fact that certain carboxylic acids split off carbon dioxide upon heating has suggested a method of attack, namely, heating the dry mercury salt of the acid or a solution of the latter in pyridine. The present paper deals only with the preparation of certain mercury compounds prepared by heating the dry mercury salts, and is merely a preliminary report on the subject.

It was found that when the mercury salt of 2,4,6-trinitro-benzoic acid was heated to  $210^{\circ}$ , a gas, which was later proved to be carbon dioxide, was given off. When the reaction was studied quantitatively, it was found that the amount of carbon dioxide lost corresponded to 2 molecules for every molecule of the mercury salt of the trinitro-benzoic acid. The product thus formed is undoubtedly 2,2',4,4',6,6'-hexanitro-mercury-diphenyl:



Analysis and the qualitative reactions of the compound seem to bear out this contention.

In the same way the mercury salt of 2,4-dinitro-phenylacetic acid upon heating decomposes into carbon dioxide and 2,2',4,4'-tetranitro-mercury-dibenzyl



The 2,2',4,4'-tetranitro-mercury-dibenzyl is insoluble in the common organic solvents; it is soluble, however, in pyridine from which it is precipitated out with ligroin. Care must be taken not to heat the pyridine solution, since this leads to the precipitation of mercury. This is characteristic also of the mercury salts of compounds which lose carbon dioxide readily. Thus the writer and A. P. Locke have found that the mercury salt of triphenyl-acetic acid when heated in pyridine solution gives rise to triphenyl-methyl peroxide.<sup>4</sup> While the dry mercury salt of triphenyl-acetic

<sup>4</sup> The reaction probably proceeds in two stages, as indicated by the equations given below:

1.  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{C}(\text{O})-\text{O}-\text{Hg}-\text{O}-\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_5)_3 \longrightarrow (\text{C}_6\text{H}_5)_3\text{C}-\text{Hg}-\text{C}(\text{C}_6\text{H}_5)_3 + 2\text{CO}_2$
2.  $(\text{C}_6\text{H}_5)_3\text{C}-\text{Hg}-\text{C}(\text{C}_6\text{H}_5)_3 \longrightarrow 2(\text{C}_6\text{H}_5)_3\text{C} + \text{Hg} \downarrow \xrightarrow{+\text{O}_2} (\text{C}_6\text{H}_5)_3\text{C}-\text{O}-\text{O}-\text{C}(\text{C}_6\text{H}_5)_3$

In the second stage of the reaction the mercury oxidizes the carbon and we get triphenyl-methyl which combines with the oxygen of the air to give triphenyl-methyl peroxide.

acid when heated gives rise to different products. This behavior of mercury salts of mono- and di-carboxylic acids, which lose carbon dioxide readily, in pyridine solution is under investigation and will be reported soon. The following types of compounds are under investigation at the present time as to the behavior of their mercury salts in pyridine solution and other solvents and upon dry heating: the phenylene oxydicarboxylic acids, the phenyl-paraffin-ketone carboxylic acids, the phenylketone mono and dicarboxylic acids, phenyl-alcohol dicarboxylic acids, the phenylene-ketone dicarboxylic acids, various substituted malonic acids, and other acids which lose carbon dioxide at their melting points or at slightly higher temperatures.

In the case of aromatic carboxylic acids which do not lose carbon dioxide readily, the mercury usually becomes attached to a carbon of the benzene ring. Although this has been known for a long time no systematic study has been undertaken as to the effect of the group already present in the molecule on the orientation of the mercury. Thus Dimroth has shown that when the mercury salt of benzoic acid was heated the mercury enters *ortho* to the carboxyl group. However, in the case of salicylic acid the mercury became attached to the carbon which is *ortho* to the hydroxyl group. The writer has investigated a number of substituted carboxylic acids, and although the work, so far as concerns the positions taken by the entering mercury, is not complete as yet, nevertheless it all points to the following rule: in the case of negatively substituted aromatic acids the mercury usually enters *ortho* to the negative group, irrespective of the position of the carboxyl group, while in the case of a positively substituted aromatic acid the mercury enters *ortho* to the carboxyl group.<sup>5</sup>

Thus, when the mercury salt of anisic acid is heated the mercury enters *ortho* to the methoxy group, as shown by the fact that when the mercury compound thus formed is treated with a solution of potassium periodide it gives 3-iodo-4-methoxybenzoic acid. In the same way in 3-nitro-4-methoxybenzoic acid and 3-nitro-4-hydroxybenzoic acid<sup>6</sup> the mercury enters *ortho* to the negative group, methoxy and hydroxyl respectively. Other substituted carboxylic acids such as *o*- and *m*-nitrobenzoic acids, 3,5-dinitro- and 2,4-dinitro-benzoic acids, the nitrosalicylic acids (2-nitrosalicylic acid [OH = 1] and 4-nitrosalicylic acid) have also been investigated, but the position taken by the entering mercury has not been established as yet, since the corresponding halogen derivatives of some of them are not recorded in the literature and it is necessary to prepare them by some other means. This work is now in progress.

*m*-And *o*-nitrobenzoic acids and other nitrobenzoic acids such as nitroanisic acid, besides giving rise to mercury compounds, in which the mercury

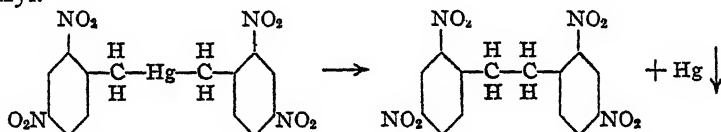
<sup>5</sup> This is not rigidly correct as will be brought out in a subsequent paper.

<sup>6</sup> Kharasch, *THIS JOURNAL*, 43, 1203 (1921).



is attached to a carbon of the benzene ring, also split off carbon dioxide especially at temperatures above 200°. Thus upon heating *o*-nitrobenzoic acid two products were obtained; one of them was found to be mercurized *o*-nitrobenzoic acid, and the other, insoluble in alkali, gave rise to nitrobenzene-*o*-mercuric chloride upon treatment with alcohol saturated with hydrogen chloride. This work is almost complete and will be reported soon.

The above mentioned method for the preparation of mercury compounds by heating the mercury salt of an acid, which loses carbon dioxide readily, would thereby enable us to replace a carboxyl group by a halogen and it is also hoped that it would have a much wider application in that by heating the mercury compound, thus formed, in the dry state or in some solvent the mercury would oxidize one of the carbons and thereby link the two carbons together. This would be especially possible in the case of the compounds where the mercury would be attached to the aliphatic residue. This observation has been made by Wolff,<sup>7</sup> incidentally, in the case of mercury dibenzyl which was found to go over into dibenzyl and metallic mercury when heated slightly above its melting point, and the writer has also observed it in the case of 2,2',4,4'-tetranitro-mercury-dibenzyl.



The writer and F. W. Stavely are engaged at the present time in working out the details and applications of this method of linking carbon to carbon.

### Experimental Part.

**The Preparation of the Mercuric Salt of 2,4-Dinitro-phenylacetic acid.**—It was found more advantageous in the preparation of the mercury salts of the substituted aromatic acids to treat a water solution of the acids with mercuric acetate, rather than by double decomposition of the sodium salts with mercuric chloride.

To a solution of 4.5 g. of 2,4-dinitro-phenylacetic acid, in 450 cc. of hot water (70°), a solution of 3.2 g. of mercuric acetate in 50 cc. of water was added in small portions, the whole being well stirred. An immediate precipitate resulted and was at once collected on a filter, washed well with water and dried *in vacuo* over sulfuric acid. Yield, 6 g. For analysis the salt was dried to constant weight *in vacuo* at 100°.

**Analysis.** Subs., 0.1844: N<sub>2</sub>, 14.00 cc. (16° and 733.2 mm.). Calc. for C<sub>16</sub>H<sub>10</sub>O<sub>12</sub>N<sub>4</sub>Hg·N, 8.59. Found: 8.66.

The compound is of a very light yellow color. When treated with sodium hydroxide solution it soon turns it dark, comparable with the behavior of 2,4-dinitro-phenyl-acetic acid. It is soluble in pyridine imparting to it a yellow color, but after a while the solution turns dark and, if warmed, metallic mercury separates. The compound has no melting point, but loses carbon dioxide when heated at 180–190° and goes over into the compound described immediately below.

<sup>7</sup> Wolff, *Ber.*, 46, 64 (1913).

**The Preparation of 2,2',4,4'-Tetranitro Mercury Dibenzyl.**—When the dry mercury salt of 2,4-dinitro-phenyl-acetic acid was heated to 180° a vigorous evolution of carbon dioxide took place and a yellow solid remained. The amount of carbon dioxide lost, as estimated by the loss in weight of the test-tube, in which the compound was contained, corresponded to two molecules for every molecule of the mercury salt of 2,4-dinitro-phenyl-acetic acid. The melting point of the compound thus obtained is 215°. After washing with acetone, in which the substance is insoluble, the melting point was raised to 235°.

For analysis the compound was dissolved in pyridine and filtered from the small amount of mercury with which it is contaminated. It was then precipitated with ligroin, and dried to constant weight *in vacuo* over sulfuric acid.

**Analysis.** Subs., 0.1280: N<sub>2</sub>, 11.30 cc. (22° and 732.5 mm.). Calc. for C<sub>14</sub>H<sub>10</sub>O<sub>8</sub>N<sub>4</sub>Hg: N, 9.97. Found: 9.83.

The compound is insoluble in all common organic solvents except pyridine and is precipitated from a solution of the latter by ligroin as a bright red powder. When the pyridine solution of the compound is heated mercury separates. It is insoluble in sodium hydroxide and also does not change color when heated with it. It melts with decomposition rather sharply at 235°, with separation of mercury.

**The Preparation of the Mercuric Salt of 2,4,6-Trinitrobenzoic Acid.**—To a solution of 5.2 g. of 2,4,6-trinitrobenzoic acid dissolved in 350 cc. of hot water, a solution of 3.4 g. of mercuric acetate in 20 cc. of water, was added. A beautiful white compound separated. The whole was then cooled, and the precipitate collected on a filter, washed several times with small amounts of cold water and dried *in vacuo* over sulfuric acid. Yield 6.1 g.

For analysis the substance was dried to constant weight *in vacuo* at 100°.

**Analysis.** Subs., 0.1078: N<sub>2</sub>, 11.50 cc. (21° and 737.8 mm.). Calc. for C<sub>14</sub>H<sub>4</sub>O<sub>10</sub>N<sub>6</sub>Hg: N, 11.81. Found: 12.03.

The salt gives the same reactions with sodium hydroxide as does trinitrobenzoic acid. It begins to give off carbon dioxide at 210° and goes over into the compound described below.

**The Preparation of 2,2',4,4',6,6'-Hexanitro Mercury Diphenyl.**—The mercury salt of 2,4,6-trinitrobenzoic acid contained in a test-tube, was heated to 210°, by immersing the latter in a sulfuric acid bath, and kept at that temperature until no more carbon dioxide was evolved. The loss in weight corresponds quantitatively to two molecules of carbon dioxide for every molecule of the mercury salt. The contents of the test-tube were then extracted with acetone. Most of the substance goes in solution and can be obtained in fairly pure condition by concentrating the acetone extract, decanting the mother liquor from the precipitate formed, and washing the latter with ether. It is best, however, to recrystallize it from a mixture of acetone and alcohol.

For analysis the substance was dried *in vacuo* at 100°.

**Analyses.** Subs., 0.5005: HgS, 0.1832. Subs., 0.1755: N<sub>2</sub>, 21.00 cc., (22° and 724.5 mm.). Calc. for C<sub>12</sub>H<sub>14</sub>O<sub>12</sub>N<sub>6</sub>Hg: N, 13.43; Hg, 31.23. Found: N, 13.27; Hg, 31.57.

The compound is white and crystalline with a faint suggestion of yellow. It is soluble in acetone, very slightly soluble in alcohol and almost insoluble in ether. It dissolves in pyridine imparting to the solution a pink color, and when heated in it, the pink color changes immediately to a green-purple. Upon exposing the solution to the air it becomes yellow and a precipitate separates which is insoluble in acetone. It melts rather sharply at 272°, and the melt does not separate any mercury when heated to 295°.

When suspended in water and treated with potassium periodide or potassium per-

bromide the mercury is not removed from the benzene ring even in the course of 10 days, as evidenced by the fact that the compound can be recovered unchanged. However, with mercuric chloride the reaction is normal. This anomalous behavior with potassium periodide is perhaps due to the fact that water does not moisten the compound.

**The Preparation of 2,4,6-Trinitro-phenyl-mercuric chloride.**—To 0.8 g. of 2,2',4,4',6,6'-hexanitro-mercury-diphenyl, suspended in 50 cc. of alcohol, 0.35 g. of mercuric chloride was added, and the whole was heated on the hot plate for 3 hours. The unchanged 2,2',4,4',6,6'-hexanitro mercury diphenyl was filtered off (0.25 g.), and the filtrate evaporated to dryness. Weight, 0.75 g. It was crystallized from alcohol.

For analysis the compound was dried *in vacuo* at 100°.

**Analysis.** Subs., 0.1937 : N<sub>2</sub>, 16.20 cc. (22° and 732.9 mm.). Calc. for C<sub>6</sub>H<sub>2</sub>O<sub>6</sub>N<sub>6</sub>ClHg: N, 9.38. Found: 9.33.

The compound is of an exceedingly light yellow color so that it appears to be almost white. It is soluble in alcohol, ether and acetone. It melts at 202° to a clear liquid.

**Preparation of 2,4,6-Trinitro-iodo-benzene and 2,2',4,4',6,6'-Hexanitro-diphenyl.**—To a suspension of 1.1 g. of 2,4,6-trinitro-phenyl-mercuric chloride in 30 cc. of water, 7 cc. of solution of potassium periodide (0.1 g. of iodine per cc.), and 5 g. of potassium iodide were added. The mixture was then agitated on the shaking machine for one hour and the precipitate collected on a filter. It was then washed well with water and dried in the oven at 100°. When completely dry the precipitate was extracted with ether. A residue remained which melted at 240° and is probably as 2,2',4,4',6,6'-hexanitro-diphenyl. The ether extract was evaporated to dryness. A very light yellow compound was thus obtained. It melted at 164–165° and was identified as 2,4,6-trinitro-iodo-benzene.

### Summary.

1. It has been shown that when the mercury salts of certain carboxylic acids are heated, carbon dioxide is split off and the mercury takes the place originally occupied by the carboxyl groups.

2. The preparation of the mercury salts of 2,4-dinitro-phenylacetic acid and 2,4,6-trinitrobenzoic acid is given as well as the compounds derived from them: 2,2',4,4'-tetranitro mercury dibenzyl, 2,2',4,4',6,6'-hexanitro mercury diphenyl, and 2,4,6-trinitro-phenyl-mercuric chloride.

3. It has been shown that when 2,4,6-trinitro-phenyl-mercuric chloride is treated with potassium periodide it gives rise to 2,4,6-trinitro-iodo-benzene, and presumably to 2,2',4,4',6,6'-hexanitro-diphenyl.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE DEPARTMENTS OF AGRICULTURAL CHEMISTRY AND AGRICULTURAL BACTERIOLOGY, UNIVERSITY OF WISCONSIN.]

## THE INFLUENCE OF CERTAIN FACTORS UPON THE CHEMICAL COMPOSITION OF SAUERKRAUT.<sup>1</sup>

BY O. R. BRUNKOW, W. H. PETERSON, AND E. B. FRED.

Received July 5, 1921.

The production of sauerkraut is an excellent illustration of the economic value of a fermentation process in the preservation of human food. It is an acid fermentation and in many respects is like that obtaining in the formation of silage, pickles, and dairy products. The art of making sauerkraut has been known and practiced for many years, but until recently little attention has been given to the different agents and factors involved in the process. Since the fermentation is a spontaneous one, it is evident that the type of flora which develops is the result of native and competing micro-organisms. Some of these organisms are desirable while others are objectionable. Although the lactic acid bacteria tend to dominate the fermentation, other bacteria or yeasts frequently develop and produce undesirable colors or flavors. The production of good kraut is, therefore, more or less a matter of chance and it is probable that inoculation with suitable bacteria will result in a better and more nearly uniform product.

The type of organisms present and the nature of the products formed in the production of sauerkraut were not studied until comparatively recent years. One of the earliest investigators in this field was Reichardt<sup>2</sup> who made an approximate analysis of sauerkraut and discussed its wholesomeness and food value.

In 1897 Conrad<sup>3</sup> made the first serious attempt to study the biochemical changes involved in the production of sauerkraut. He made a bacteriological examination of both cabbage and sauerkraut, and isolated two yeasts and an organism, *Bacterium brassicae acidae*, which he regarded as the chief agent responsible for the fermentation. With this bacterium he carried out a number of fermentations of cabbage and various carbohydrates to determine its fermentation characteristics, and its usefulness in the production of sauerkraut. Besides his work on the organisms of sauerkraut, he has supplied the most complete chemical analysis of this product that has been published. He reported the production of formic, acetic, butyric, and lactic acids, ethyl alcohol, carbon dioxide, methane, and hydrogen as a result of fermentation processes. The lactic acid was found to be inactive, and tests for acetone and mercaptans were negative. About the same time as Conrad's publication, a paper by Krause<sup>4</sup> appeared in which the acidity of sauerkraut was asserted to be due almost entirely to lactic acid with only a trace of acetic acid.

<sup>1</sup> Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

<sup>2</sup> Reichardt, *Z. Nahrungsm.*, 5, 43 (1891).

<sup>3</sup> Conrad, *Arch. Hyg.*, 29, 56 (1897).

<sup>4</sup> Krause, *Apoth. Ztg.*, 12, 88 (1897).

In 1905 Wehmer<sup>5</sup> published two long papers on the types of organisms present in sauerkraut and the effect of inoculation, temperature, salts, and water on the quality of the kraut. He isolated and studied the fermentation characteristics of 2 bacteria and 5 yeasts. The organism which he considered as most important in the formation of the acid in sauerkraut was a short rod-form, *Bacterium brassicae*, which grew under both aerobic and anaerobic conditions and produced a high concentration of acid. The other type of bacterium was a long slender rod and produced only a small quantity of acid. The 5 yeasts were divided into 2 classes: bottom yeasts which produced gas and alcohol, and surface yeasts which destroyed the acids that had been formed earlier in the fermentation.

In 1905 Perekalin<sup>6</sup> isolated an organism from kraut, which he deemed typical of sauerkraut because of its growth and persistence in a highly acid medium.

In 1909 Gruber<sup>7</sup> isolated an organism *Pseudomonas brassicae acidae*, which when used in pure cultures gave a kraut of good flavor and shortened the period of fermentation.

Round<sup>8</sup> published a short note in 1916 calling attention to the large number of organisms present in the vats of commercial plants, and concluded that bacteria alone are concerned in a proper fermentation.

The papers of Henneberg<sup>9</sup> published in 1917, give a very extensive discussion of the manufacture of sauerkraut. In his bacteriological work on the flora of kraut he found 8 different yeasts, 7 strains of lactic acid bacteria, 2 colon types, 1 acetic acid type, and 5 molds. The bacteria which he considered the most important were *Bacterium lactis acidii*, and *Bacillus cucumeris fermentati*, a long rod related to Wehmer's *Bacterium brassicae*. The most important yeast was a small celled form, *Saccharomyces panis fermentati*. He studied the influence of inoculation with pure cultures of organisms upon the fermentation of sauerkraut, and obtained the best results by inoculating with a mixed culture of lactic acid bacteria and yeasts.

Nelson and Beck<sup>10</sup> published a short article in 1918 on the fermentation products found in sauerkraut. They reported the volatile acids to consist largely of acetic and a small proportion of formic and propionic acids. The alcohols were found to be mainly ethyl alcohol and a small amount of propyl alcohol.

In recent papers Le Fevre<sup>11</sup> has discussed the effect of temperature and the use of pure cultures on the production of sauerkraut. While inoculation aids in the fermentation of the cabbage, he considered temperature to be the most important factor in bringing about a rapid and satisfactory fermentation.

From the foregoing review of the literature it is clear that little is known concerning the kinds and amounts of fermentation products contained in sauerkraut.

### Experimental.

The object of this work included the determination of the main products formed in sauerkraut during a normal fermentation and the influence of

<sup>5</sup> Wehmer, *Centr. Bakt. Parasitenk.*, II Abt., 14, 682, 781 (1905).

<sup>6</sup> Perekalin, *ibid.*, II Abt., 14, 225 (1905).

<sup>7</sup> Gruber, *ibid.*, II Abt., 22, 555 (1909).

<sup>8</sup> Round, *J. Bact.*, 1, 108 (1916).

<sup>9</sup> Henneberg, *Die Deut. Essigind.*, 20, 133, 141, 152, 160, 166, 176, 184, 192, 199, 207, 215, 223 (1916).

<sup>10</sup> Nelson and Beck, *THIS JOURNAL*, 40, 1001 (1918).

<sup>11</sup> Le Fevre, *The Canner*, 48, 176 (1919); 50, 161 (1920); 52, 146 (1921).

inoculation on the products formed, and quality of the sauerkraut. The effect of salt concentration on the quality of the sauerkraut was also noted.

Most of the kraut was made under laboratory conditions, but two tanks were made on a commercial scale; one of these was inoculated with a pure culture of organisms and the other was left uninoculated in order to serve as a control.<sup>12</sup>

The kraut made under laboratory conditions consisted of 6 series of fermentations, comprising 61 separate samples. In each series 2 containers were always used as controls. In these the usual amount of salt (2-2.5%) was used and the cabbage allowed to ferment normally. To the other containers in the series pure cultures of organisms were added.

The fermentations were carried out in glass percolators of 2-liter capacity. The bottom of each percolator was fitted with a 1-hole rubber stopper, through which was passed a glass tube closed at the lower end with a piece of rubber tubing and a pinchcock. Some glass wool was placed over the end of the glass tube inside the percolator to prevent the cut cabbage from plugging the tube. This arrangement allowed the brine to be readily drawn from the bottom of the container without disturbing its contents. Fifteen hundred g. of cut cabbage, the weight usually taken, was prepared by removing the outer leaves and the cores of the cabbage and cutting with a hand cutter. The salt was mixed with the cabbage in a large pan and when cultures of organisms were used they were added at this time to insure uniform distribution. The whole was then transferred to the percolator. A large paraffined cork, slightly smaller than the inside diameter of the percolator, was placed over the cabbage, and this was held down by a bottle containing 1 kg. of mercury or sand.

The main chemical changes in the production of good sauerkraut involve the destruction of the sugars in the cabbage, resulting in the formation of volatile and non-volatile acids, alcohol, and mannitol. A decrease in the toughness of the cabbage and the development of a translucent appearance accompany this change.

Observations of the color and texture of the cabbage, as well as titrations of the brine were made daily during the first 6 to 8 days of the fermentation period, after which they were made at longer intervals. Titrations were made on the brine from the top and bottom of several containers to determine whether there existed any difference in the acidity. In one series stained mounts were made daily, and at the end of the fermentation, of the brine from the control and of the brine inoculated with *B. lactis acidii*. In several experiments counts were made of the number of micro-organisms present in the brine. From the data secured from a study of commercial kraut, inoculation appeared to increase the number of bacteria present,

<sup>12</sup> The authors desire to express their appreciation to the Onalaska Canning Company, Onalaska, Wisconsin for their cooperation in carrying out this part of the work.

but this was not true of the kraut made in the laboratory. The number of micro-organisms present in the samples of kraut investigated varied from about 500,000 to 91,000,000 per cc. of brine.

The rate at which the fermentation proceeds can be measured by titrating portions of the brine from day to day, and can be influenced by the temperature under which the fermentation takes place and the flora which is present.

The curves in Fig. 1 represent typical titrations of the rate and amount of acid developed and the influence of inoculation with pure cultures of organisms. It will be seen that in the case of the inoculated kraut there is an increase in the development of acidity over the control during the first few days. A fall in the amount of acid on about the tenth or twelfth day seemed characteristic of both fermentations. This decline was

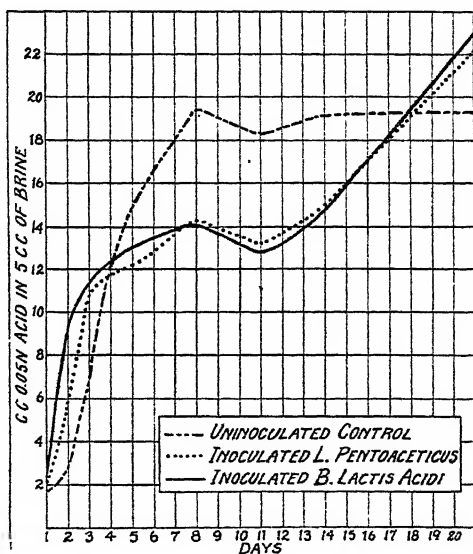


Fig. 1.—The influence of inoculation upon the development of acidity.

followed by another distinct rise in a few days. This second rise as well as the first one was invariably more pronounced in the inoculated fermentations than in the control. After the twenty-fifth day there was seldom much change in the amount of acid in the brine from the bottom of the container. However, there is always a marked decrease in the acidity of brine from the top, due to the destruction of the acid by *mycodermae*. The acidity at the top and bottom of the percolators was followed closely in several fermentations and it was found that during the first four days of the fermentation period there was practically no difference between the two. On the fifth day there was an increase in the acidity of the brine

from the top over that from the bottom except in one case where a great many *mycodermae* had developed. The acidities of the brine from the top exceeded those of the brine from the bottom until the fourteenth day when they generally fell below those of the bottom brines.

TABLE I.  
THE INFLUENCE OF SALT ON THE FERMENTATION OF KRAUT.

Series.	Salt.	Temper- ature.	Inocu- lation.	Age when opened.	Titratable acidity in 5 cc. of brine expressed as 0.05 N acid.		Quality of Product.
					When opened.	Maximum.	
	%.	° C.		Days	Cc.	Cc.	
I <sup>a</sup>	3.5	20-23	none	31	17.0	17.1	Taste and odor good, texture tough.
I <sup>a</sup>	3.5	20-23	41-11	31	15.5	15.6	
II <sup>b</sup>	2.0	16-26	none	23	15.9	15.9	Taste, odor, and texture good.
II <sup>b</sup>	2.0	16-26	41-11	23	16.0	16.0	
II <sup>b</sup>	0.0	16-26	none	20	14.3	14.3	Taste and odor disagreeable, textur too soft.
II <sup>b</sup>	0.0	16-25	41-11	23	12.8	19.6	Taste very sour and bitter, odor bad, texture too soft.
VII <sup>c</sup>	2.5	16-25	none	28	18.4	19.7	Taste, odor, and texture very good.
VII <sup>c</sup>	2.5	16-25	<i>B. lactis acidi</i>	28	17.5	19.0	Excellent taste, odor, and texture.

Dates: <sup>a</sup> October 9, 1920; <sup>b</sup> October 25, 1920; <sup>c</sup> March 21, 1921.

**Influence of salt concentration.**—It has been reported by some investigators that good kraut can be made without salt. With this idea in view 4 fermentations were carried out in the absence of salt. Two were inoculated with a pure culture of *Lactobacillus pentoceticus* while the other two were left uninoculated. All 4 made a product having a bad odor, a sour and bitter taste, and a dark color. The data in Table I show that those inoculated produced higher acidity than the controls. This would be expected because Culture 41-11 is an organism forming a high degree of acidity.

In another series the salt content was increased from 2.0 to 3.5%. Although the flavor was good, a salty taste was predominant and the kraut was tough. In this experiment the control krauts developed a higher acidity than those which were inoculated with pure cultures. The reason for this is probably due to the sensitiveness of Culture 41-11 to a high salt concentration.

For the remaining series a concentration of 2 or 2.5 % of salt based on the weight of the cut cabbage was used and at either concentration very good results were secured with and without inoculation.

**Influence of inoculation.**—In Table II the results of a large number of inoculations with pure cultures are given; 50 cc. of a 48-hour yeast-water culture was used for each 1500 g. of cut cabbage, and to the controls 50 cc. of distilled water was added in place of the inoculating material.



Cultures 41-11 and 118-8 are the same type of organism and are named *Lactobacillus pentoaceticus*. They are essentially acid producers and ferment such sugars as xylose, arabinose, glucose, galactose, mannose, and fructose with the formation of lactic and acetic acids, ethyl alcohol, carbon dioxide, and mannitol. Cultures 52-7 and 124-1 were isolated from sauerkraut during this study; Culture 52-7 has the same characteristics as 41-11; 124-1 is a pentose-fermenter but does not belong to the same group as 41-11. Cultures 52-3 and 85 are yeasts and were isolated during this study from commercial sauerkraut that had turned red. These yeasts were found to produce red pigments when grown on agar plates. A report of red kraut and the factors influencing its formation is given in another paper now in press. The mixed culture was isolated from sauer-

TABLE II.

THE INFLUENCE OF INOCULATION ON THE FERMENTATION OF KRAUT.

2% of Salt used in Series IV and V, and 2.5% in Series VI.

Temperature 17-23° in Series IV; 21-23° in Series V; 16-25° in Series VI.

Series.	Inoculation.	Age when opened.	Titratable acidity in 5 cc. of brine expressed as 0.05 N acid.		Quality.
			When opened.	Maximum.	
IV	none	33	20.7	20.7	Flavor, odor and texture good.
	118-8	33	21.8	21.8	Texture good; flavor fair.
	<i>B. lactis acidi</i>	33	24.1	24.1	Excellent flavor and color; texture and odor good.
	<i>B. bulgaricus</i>	33	15.6	15.6	Developed red color; flavor fair.
	52-7	33	23.3	23.3	Taste, odor and color excellent.
	52-3	33	13.9	13.9	Developed red color; flavor poor.
	(52-3 +)	33	15.0	15.0	Flavor, odor and texture, fair.
	(52-7 )				
V	<i>B. lactis acidi</i>	31	19.1	19.1	Excellent flavor, color and texture.
	124-1	31	15.2	16.8	Developed red color; taste fair.
VI	none	28	18.4	19.7	Taste, color and texture good.
	124-1	28	12.3	15.2	Developed pink color; taste fair.
	<i>B. lactis acidi</i>	28	17.5	19.0	Flavor, odor and color excellent; texture good.
	<i>B. lactis acidi</i>	14	15.4	15.4	Taste, odor and color excellent; texture fair.

kraut but the characteristics of the organisms present were not determined. Strains of *B. lactis acidi*, and *B. bulgaricus* were also used.

From the remarks in Table II on the quality it will be seen that there are certain organisms which uniformly produce good kraut when used in pure culture. In the commercial kraut it was thought that Culture 41-11 produced a grade of sauerkraut superior to the uninoculated, but this could not be duplicated in the laboratory fermentations. The one organism which was always found to produce an especially good kraut was a

strain of *B. lactis acidii*. This organism was used in 3 series and produced the best kraut of the series each time. The product has a desirable appearance, a mild, pleasant odor and taste, and good texture. Although it does not produce acid as rapidly as some of the other organisms, nevertheless, kraut inoculated with this organism was declared ready to can after fermenting for 14 days. In contrast to the favorable results obtained with *B. lactis acidii* was the production of pink kraut whenever Culture 124-1 was used for inoculating. Culture 124-1 is a high acid-forming organism and appears to favor the development of the yeasts which produce the red pigment. Aside from this the kraut was of fair quality.

From the brine of several inoculated and uninoculated fermentations microscopic mounts were made. In nearly every case where pure cultures were used it was found that these organisms predominated throughout the fermentation period. In the last series of fermentations the flora was watched closely in both the uninoculated and inoculated kraut. Stained microscopic mounts were made daily on the brine. It was found that in the brine from the control the organisms were yeasts and long rod, short rod, and coccus forms of bacteria. The rod forms were about equal in distribution and were less numerous than the coccus forms during the first 7 or 8 days of the fermentation. After this time the long rod forms increased in number and were predominant at the end of the fermentation period.

In several of the series of experiments wet microscopic mounts were made and examined at the time the sauerkraut was removed from the containers. A comparison of the number of yeasts with that of the bacteria could be roughly determined in this manner and whenever yeasts were in excess over bacteria or were predominant in the field the kraut was invariably poor. It was also true that whenever the kraut turned red large numbers of yeasts were found to be present.

**Chemical Analyses.**—The kraut was removed from the containers and the brine pressed out with a powerful hand press. A small sample of the kraut was dried at 105° to constant weight to obtain the moisture content. A sample of the brine was used for determining the total titratable acidity and the remainder was used for determining the volatile acid, non-volatile acid, and alcohol. The methods outlined by Fred, Peterson and Davenport<sup>13</sup> were used in determining these constituents. A portion of the brine was distilled with steam and the volatile acids were titrated with 0.1 N barium hydroxide solution. The residue from the steam distillation was placed in a Kutscher and Steudel<sup>14</sup> apparatus and extracted with ether to obtain the non-volatile acids. The alcohols were determined in another portion of the brine by saturating it with sodium chloride and

<sup>13</sup> Fred, Peterson and Davenport, *J. Biol. Chem.*, 39, 347 (1919).

<sup>14</sup> Kutscher and Steudel, *Z. physiol. Chem.*, 39, 473 (1903).

distilling the alcohol which was in turn oxidized to the corresponding acid with potassium dichromate. The acid formed was distilled off and titrated with 0.1 *N* barium hydroxide solution. In all of the determinations

TABLE III.  
ANALYSIS OF SAUERKRAUT SHOWING THE CHIEF FERMENTATION PRODUCTS.

Sample number and treatment.	Moisture.	0.1 <i>N</i> acid in	Volatile	Non-volatile	Alcohol
		100 cc. of brine.	acid as acetic in 100 g. of kraut.	acid as lactic in 100 g. of kraut.	ethyl in 100 g. of kraut.
	%.	Cc.	%.	%.	%.
<i>Commercial sauerkraut</i>					
Inoculated with 41-11	90.0	144.7	0.233	1.220	0.843
Uninoculated <sup>a</sup>	88.0	147.5	0.244	1.254	0.860
Uninoculated <sup>b</sup>	90.6	140.0	0.224	0.929	0.658
<i>Laboratory sauerkraut</i>					
Control	91.6	158.0	0.315	1.195	0.371
Inoculated with 52-7	91.7	147.0	0.222	0.986	0.408
<i>B. lactis acidi</i>	90.3	173.0	0.265	1.259	0.267
<i>B. lactis acidi</i>	92.6	181.0	0.255	1.304	0.249
41-11, no salt	92.9	129.0	0.442	0.607	0.267
41-11	93.4	166.5	0.272	0.970	0.436

<sup>a</sup> This kraut had developed a pink color.

<sup>b</sup> This kraut was of good quality.

the barium salts formed were evaporated to dryness and used for the identification of the acids and alcohols. The results of a number of analyses on commercial and laboratory kraut are given in Table III.

The data show a fair agreement in the case of the uninoculated krauts, both laboratory and commercial, in all the products except in the alcohols. It has been shown by Peterson and Fred<sup>15</sup> that alcohol is easily lost by evaporation from a fermenting solution. Since the containers were not covered, it may well be assumed that alcohol was lost during fermentation while gases were escaping from the brine. Cultures 52-7 and 41-11 are the same type of organism and produce the same products. They are essentially high acid- and alcohol-producing organisms and a glance at the table will show that these products were characteristic of the fermentation. In kraut inoculated with *B. lactis acidi* large amounts of lactic acid would be expected. The data in the table are in harmony with this view, although the presence of volatile acid and alcohol indicate the activity of other organisms.

The analysis of kraut containing no salt shows an unusually high content of volatile acid with a very low content of non-volatile, and very little difference in the amount of alcohol. The absence of salt has evidently favored the growth of volatile acid and alcohol-producing organisms. The acids and alcohol from this fermentation were not identified, but butyric acid was suggested by a very disagreeable taste and odor. Butyric acid has been reported by Wehmer<sup>16</sup> in kraut made without salt.

<sup>15</sup> Peterson and Fred, *J. Biol. Chem.*, 42, 273 (1920).

**Identification of Products.**—In the identification of the volatile acids three methods were used: the fractional precipitation and analysis of the silver salts; the Duclaux analysis; and the determination of the barium content of the barium salts. The barium salts of the volatile acids were dissolved in water, filtered from any insoluble material, and the filtrate made up to a definite volume. The qualitative method of Orla-Jensen<sup>16</sup> was used to determine what acids were present. From the solution of the barium salts the acids were fractionally precipitated as the silver salts by the addition of 2 *N* silver nitrate. The silver salts of the acids of highest molecular weight come out first and contain the lowest percentage of silver. After precipitation, the several fractions of silver salts were dried, weighed, and ignited to determine the silver content. In each fraction

TABLE IV.

DISTILLING CONSTANTS OF VOLATILE ACIDS OBTAINED BY DUCLAUX METHOD.

Source of acid.	Cc.	Fraction.									
		10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
Purified acetic acid		7.4	15.2	23.6	32.2	41.4	51.0	61.3	72.4	85.1	100.0
Alcohol from inoculated kraut		7.6	15.6	23.8	32.5	41.5	51.0	61.2	72.3	84.8	100.0
Alcohol from uninoculated kraut		7.4	15.2	23.4	32.0	40.9	50.5	60.9	71.9	84.4	100.0
Volatile acid from uninoculated kraut		7.7	15.8	24.3	33.0	42.2	51.7	64.0	73.2	85.5	100.0
Volatile acid from 50 cc. fraction of uninoculated volatile acid		7.6	15.6	23.9	32.6	41.7	51.2	61.4	72.6	85.0	100.0

TABLE V.

BARIUM CONTENT OF BARIUM SALTS.

Source of acid.	Weight of barium salts. G.	Weight of barium sulfate. Found. G.	Calculated. G.	Salt assumed in calculation.
Alcohol distillate	0.3472	0.3121	0.3172	Barium acetate
inoculated with 41-11		0.2590	0.2643	
Alcohol distillate uninoculated	0.4726	0.4308	0.4318	
Volatile acids uninoculated	0.5304	0.4780	0.4846	
Volatile acids from 50 cc. fraction	0.3217	0.2980	0.2939	Barium lactate
		0.2934	0.2947	
Non-volatile acids uninoculated	0.3038	0.2194	0.2248	
		0.2192	0.2236	
Non-volatile acids inoculated with 41-11	0.3814	0.2787	0.2822	
		0.2846	0.2878	

except the first, which was slightly contaminated with chlorides, the percentage of silver was always in very good agreement with that required for pure silver acetate. This result led to the conclusion that only acetic acid was present, and the correctness of this conclusion was proven by a determination of the barium content of the barium salts, and by a Duclaux

<sup>16</sup> Orla-Jensen, *Landw. Jahrb. d. Schweiz*, 18, 314 (1904).

determination on the free acid. It will be seen from Table IV that the Duclaux constants are in very good agreement with those obtained with our apparatus on pure acetic acid. Table V shows the barium content to be very close to the calculated value for pure barium acetate. From these results it is believed that acetic acid was the only volatile acid present.

This was further substantiated by liberating 50 cc. of 0.1 *N* acid from the barium salt by the addition of an equal amount of sulfuric acid. The solution was distilled with steam and the acids in the distillate subjected to a Duclaux determination. Since the acids of higher molecular weight are more volatile than acetic, they should have been collected by this method in excess over acetic. However, it will be seen from Table IV that the results of the Duclaux determination are almost identical with those of the first analysis and are in good agreement with those for pure acetic acid. The barium content was determined on the barium salts of this fraction and it was found to agree closely with the barium content in the first analysis and the theoretical value for pure barium acetate. From these results apparently acetic acid was the only volatile acid present.

The identification of the volatile acid formed from the oxidation of the alcohol was carried out in the same manner as the identification of the volatile acid in the kraut. The results of the Duclaux determination appear in Table IV, and the barium content of the barium salt is given in Table V. Since these are in such good agreement with pure acetic acid it is concluded that only acetic acid was present and, therefore, ethyl alcohol was the only alcohol present.

In identifying the non-volatile acids the barium salts were dissolved in water and filtered from any insoluble material. After the filtrate was evaporated to about 30 cc. it was made up to 300 cc. with absolute alcohol. If any barium succinate were present, it would be precipitated at this point because it is insoluble in 90% alcohol. The only precipitate which formed was a sticky wax-like substance which was readily soluble in small amounts of water. The alcohol solution of the barium salt was then filtered, made

TABLE VI.  
WATER OF CRYSTALLIZATION IN ZINC LACTATE.

Source of acid.	Wt. of zinc lactate used.		Water lost.		Water in Zn (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> + 3H <sub>2</sub> O. %
	G.	G.	%.	%.	
Uninoculated kraut (1)	0.8780	0.1597	18.26		18.17
(2)	2.3730	0.4334	18.19		18.17
Kraut inoculated with 41-11	(1) 0.9568	0.1726	18.04		18.17
	(2) 0.7485	0.1356	18.11		18.17

up to volume and aliquot portions were taken for determining the barium content of the barium salts. The data are given in Table V and will be found to agree very well with the barium content of pure barium lactate. The remainder of the alcoholic solution of the barium salts was used for

making the zinc salts. This was done by distilling the alcohol and taking up the barium salts in water. The zinc salts were then formed by the addition of 0.5 *N* zinc sulfate solution. After the barium sulfate was filtered off the filtrate was concentrated to a small volume (20–30 cc.) from which the zinc lactate was allowed to crystallize. The kind of lactic acid present was determined by obtaining the water content of the zinc lactate. From Table VI it will be seen that these results are in very good agreement with those of the zinc salts of inactive lactic acid. From these data it appears that inactive lactic acid is the form of acid produced in the fermentation.

**Mannitol.**—One quantitative determination of mannitol was made in the following manner. The residue in the extraction apparatus after the non-volatile acids had been removed was freed from ether and neutralized with barium hydroxide. The precipitate of barium sulfate was filtered off and the filtrate evaporated to dryness on asbestos, from which the mannitol was extracted, by continuous extraction with boiling absolute alcohol. This extraction was continued until a 12-hour extraction recovered no trace of mannitol. The mannitol is insoluble in cold absolute alcohol and crystallizes out readily. Absolute alcohol is an improvement over 90 or 95% alcohol because it extracts the mannitol practically free from salt. It is difficult to separate mannitol from sodium chloride by crystallization if they are extracted together.

Feder<sup>17</sup> used 90% alcohol for extracting the mannitol and states that his product contained about  $\frac{1}{3}$  salt. The results obtained are much lower than those reported by other investigators. In four determinations Feder found from 0.8 to 1.16%, while Nelson and Beck<sup>10</sup> found from 1.9 to 2.5% of mannitol. In a natural fermentation such as sauerkraut the amount of mannitol present is largely a matter of chance. It is formed by certain bacetria which ferment a part of the fructose to acids, etc., and at the same time reduce another part of the fructose to mannitol. The mannitol thus formed may subsequently be destroyed by the bacteria that produced it or by many other bacteria which use mannitol as a source of carbon. Cabbage contains approximately 4% of sugar, and it is probable that not more than half of this is fructose. Since the highest conversion of fructose to mannitol reported by Gayon and Dubourg,<sup>18</sup> was 66%, the above results appear very high. By extracting with absolute alcohol only 0.27% of mannitol was found. This had a melting point of 165°.

### Summary.

From the results of 61 experiments it appears that inoculation with certain organisms produces a better grade of sauerkraut than is produced

<sup>17</sup> Feder, *Z. Nahr. Genussm.*, 22, 295 (1911).

<sup>18</sup> Gayon and Dubourg, *Ann. inst. Pasteur*, 15, 527 (1901).

by a natural fermentation. Although an improved product was obtained with several different organisms the only one which was consistently better than the control was *B. lactis acidi*. The data are not extensive enough to recommend the use of inoculation on a commercial scale. Further experiments are needed.

That the organisms used for inoculation dominated the fermentation was indicated by microscopic mounts made from the brine at intervals throughout the fermentation period. A chemical analysis also showed the characteristic products normally formed by these organisms.

The presence of large numbers of yeasts may cause red kraut, and undesirable flavors.

The best kraut was obtained when approximately 2.0% of salt was used. With concentration above 3.0% the kraut was tough and too salty.

The chief products formed in the fermentation of kraut are lactic acid, acetic acid, and ethyl alcohol. Mannitol in varying amounts may also be formed, depending upon the type of organisms present. These same products occur in a natural fermentation, but the relative amounts can be influenced by inoculation.

MADISON, WISCONSIN.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]  
2-PHENYLQUINOLINE-4-CARBOXYLIC ACID-6-ARSONIC ACID.<sup>1</sup>

By J. R. JOHNSON WITH ROGER ADAMS.<sup>2</sup>

Received November 28, 1921.

In connection with the investigations being carried on in this laboratory on arsenic compounds of possible therapeutic value, 2-phenylquinoline-4-carboxylic acid-6-arsonic acid has been prepared. It is formed by the action of pyruvic acid on benzaldehyde and arsanilic acid, and is the simplest of a large number of compounds which may be made in a similar manner. This communication is merely a preliminary notice of a rather extensive research which has been carried out in this laboratory during the past 2 years upon various quinoline arsonic acids, their reduction products and other derivatives.

When aniline<sup>3</sup> and some of the simplest aniline derivatives are treated with pyruvic acid and an aromatic aldehyde, it is generally possible to obtain both a phenyl-cinchoninic acid derivative and a phenyl-diketo-

<sup>1</sup> The expenses involved in the research described in this communication were partially defrayed by funds granted by the United States Interdepartmental Social Hygiene Board.

<sup>2</sup> This is a description of a portion of the laboratory work submitted by J. R. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

<sup>3</sup> *Ber.*, 41, 3884 (1908).

pyrrolidine derivative. With the arsonated anilines in alcoholic suspension or solution, the reactions seem to run chiefly to the quinoline derivatives. 2-Phenylquinoline-4-carboxylic acid-6-arsonic acid is readily soluble in alkali hydroxides and carbonates and ammonium hydroxide and these solutions give precipitates with the salts of many of the heavy metals. The fact that the substance described gives off one mole of carbon dioxide on heating, and in addition forms a trisodium salt, proves without question its constitution.

### Experimental.

A mixture of 21.7 g. (1 mole) of arsanilic acid, 10.6 g. of benzaldehyde (1 mole) and 200 cc. of absolute alcohol is heated to boiling under reflux on a steam-bath. After a short while most of the arsanilic acid passes into solution and 8.8 g. of pyruvic acid (1 mole) is now added. The solution is heated to boiling for  $3\frac{1}{2}$  to 4 hours, and then filtered hot to remove a slight amount of insoluble material. On cooling the filtrate, a yellow precipitate results which is filtered, washed sparingly with cold alcohol, finally with ether and then dried *in vacuo*. The crude 2-phenylquinoline-4-carboxylic acid-6-arsonic acid thus obtained is pale yellow in color and melts with complete decomposition at  $180-183^{\circ}$ . After one crystallization from ordinary alcohol and washing with alcohol followed by ether, the substance is pure and is then a cream colored powder which starts to darken at about  $180^{\circ}$  and melts with decomposition at  $186-187^{\circ}$  (corr.).

The compound forms a neutral disodium salt and a slightly alkaline tri-sodium salt. From a solution of the disodium salt, copper sulfate precipitates a green salt; silver, lead, mercurous, mercuric, cadmium nitrates light yellow salts and cobalt and ferric nitrates reddish brown salts. In order to show that the compound is a quinoline derivative, its decomposition by heating was carried out in the following way. A definite weight of the substance was suspended in ethyl benzoate and then heated to boiling for 20 minutes. Enough carbon dioxide was evolved to correspond to one mole. Owing to the fact that a gummy material is produced during the decomposition, the reaction was not as complete as might be desired, so the analytical results showed between 5 and 10% too small an amount of carbon dioxide for the amount of substance used. Phenyl-diketopyrrolidine derivatives do not decompose in this manner.

The arsenic was determined by Ewins' method<sup>4</sup> the nitrogen by the Kjeldahl method and the carbon by the Parr total carbon method.<sup>5</sup>

Subs., 0.5001, 0.5005 :  $\text{CO}_2$ , 563.5 cc., ( $28.5^{\circ}$ , 746 mm.), 565.3 cc. ( $30.0^{\circ}$ , 746 mm.)

Subs., 0.1999, 0.2023 : 14.46 cc., 14.49 cc. 0.0736 N I.

<sup>4</sup> Ewins, *J. Chem. Soc.*, 109, 1356 (1916).

<sup>5</sup> Parr, *THIS JOURNAL*, 26, 296 (1904).



Subs., 0.5001, 0.5034. 18.32 cc., 18.36 cc. 0.0699 *N* HCl.

Calc.  $C_{14}H_{12}O_2NAs$ : C, 51.47; As, 20.10; N, 3.75. Found C, 51.54, 51.20. As 19.97, 19.77; N, 3.58, 3.57.

URBANA, ILLINOIS.

### NOTE.

**Bromo-quinaldines.**—6-Bromo-quinaldine has been prepared by Barton and MacCollum<sup>1</sup> by the condensation of *p*-bromo-aniline and acetaldehyde, but, this method not proving satisfactory for our purposes, the following method was used.

Ten g. of *p*-bromo-aniline was mixed with 13 g. of conc. hydrochloric acid. The mixture was cooled and 6 g. of paraldehyde was added. Condensation was brought about by heating the mixture on a boiling-water bath during 3 hours. Five hundred g. of water was added, and the aldehyde resin coagulated by heating on the water-bath. The clear liquid was then poured off, made alkaline and distilled with steam.

The crude mixture thus obtained was heated with an equal bulk of acetic anhydride at 100° for 15 minutes, the excess of acetic anhydride removed by boiling with alcohol and subsequently evaporating the ester, and the solid extracted with chloroform in the cold and crystallized from light petroleum ether.

**6-Bromo-quinaldine Methiodide.**—A mixture of 10 g. of 6-bromo-quinaldine and 6.4 g. of methyl iodide was heated for 24 hours in a sealed tube at 79–80°. A yellow crystalline solid was obtained which, when crystallized from alcohol, gave 12 g. of greenish-yellow needles melting at 237° (decomp.).

*Analysis.* Subs., 0.3110: AgI, 0.1995. Calc. for  $C_{11}H_{11}BrNI$ : I, 34.9. Found: 34.7.

**6-Bromo-quinaldine Ethiodide.**—A mixture of 16.1 g. of 6-bromo-quinaldine and 11.7 g. of ethyl iodide was heated in a boiling-water bath for 36 hours. The product was purified as above. M. p. 218°.

*Analysis.* Subs., 0.3000: AgI, 0.1860. Calc. for  $C_{12}H_{12}BrNI$ : I, 33.6. Found: 33.5.

*m*-Bromo-aniline was condensed with paraldehyde in the same way and the crude oily product diazotized and distilled with steam to get rid of the unchanged primary amine. A yellow solid was obtained (11 g.) which was heated with 3.5 cc. of nitric acid, sp. gr. 1.42, in 20 cc. of water. Yellow crystals of bromo-quinaldine nitrate were obtained and the base precipitated from an aqueous solution with ammonia. It was recrystallized from petroleum ether (60–80°), when white leaflets melting at 77° were obtained.

*Analyses.* Subs., 0.1735: CO<sub>2</sub>, 0.3470; H<sub>2</sub>O, 0.636. Calc. for  $C_{10}H_8BrN$ : C, 54.3; H, 3.7. Found: C, 53.97; H, 3.99.

Subs., 0.2393: AgBr, 0.2015. Calc. for  $C_{10}H_8BrN$ : Br, 35.98. Found: 35.83.

When condensations are made with paraldehyde and *m*-bromo-aniline, it is evident that two bromo-quinaldines may be obtained, the bromine atom in the *meta* position with respect to the amino group in the primary base occupying the 5-, or 7-, position in the bromo-quinaldine. Only one of these two possible isomers has been isolated. The position of the bromine atom has been left undetermined for the present.

The ethiodide was prepared in the same way as the ethiodide of 6-bromo-quinaldine, m. p. 217°. The nitrate melts at 102°. The salts of the other two common mineral acids are very soluble in water. The double salts with zinc chloride, mercuric chloride and stannic chloride have been prepared by boiling together solutions in hydrochloric acid

<sup>1</sup> Barton and MacCollum, *THIS JOURNAL*, 26, 704 (1904).

of the base and the respective salts: (a) *bromo-quinaldine zinc chloride*, colorless needles, soluble in water, m. p. 268°; (b) *bromo-quinaldine stannic chloride*, colorless leaflets, insoluble in water; (c) *bromo-quinaldine mercuric chloride*, colorless needles, soluble in water, m. p. 245°; (d) *bromo-quinaldine picrate*, yellow leaflets insoluble in alcohol, crystallized from acetone, m. p. 207°.

The above preparations were carried out during the course of an investigation on the modifications in photographic sensitiveness brought about by the introduction of bromine in the benzene ring of the quinaldine nucleus of pinaverdol and pinacyanol.

The author's thanks are due to Professor W. J. Pope of Cambridge University who directed this work, and to Mr. W. H. Mills, for their advice and guidance.

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Received April 6, 1921.

## NEW BOOKS.

**Tables of Physical and Chemical Constants and Some Mathematical Functions.** Fourth edition. By G. W. C. KAYE, O. B. E., M. A., D. Sc., The National Physical Laboratory, and T. H. LABY, M. A., Professor of Natural Philosophy, The University of Melbourne. Longmans, Green and Company, 39 Paternoster Row, London; Fourth Avenue and 30th Street, New York; Bombay, Calcutta and Madras. 1921. iii + 161 pp. 16.5 × 25 cm. Price \$4.00.

The selection of data to be included in a small handbook of convenient size and moderate price to be used both by physicists and chemists is a difficult problem. The fact that a fourth edition of these Tables, first published in 1911, has now appeared is evidence that the selection there made was a wise one. Nevertheless, the Tables are much more complete from a physical than from a chemical standpoint. For instance, information as to chemical equilibria, electromotive forces, the vapor pressures of solutions, and reaction velocities is almost wholly lacking. We are sure that a still wider usefulness for the book could be secured by a revision and extension of its chemical data.

A number of alterations and additions have been made in this issue. Matter relating to the figure of the earth, the absolute determination of the acceleration of gravity, and more extended tables of the relative value of that constant have been added. The chemical data have been recalculated, using the international atomic weights. Some 700 additions and alterations in the physical constants of chemical compounds have been made. The authors state that the published values of these constants have been critically examined, and what appear to be the more accurate values for the chemical compounds included in these pages, have been used. Many of the heat tables have also been revised and amplified. The modernity of the book is demonstrated by the addition of tables of atomic

numbers, spark-gap voltages, X-ray wave lengths and terrestrial magnetic constants. The effect has been to increase the size of the book by 8 pages.

All told, this book represents a surprisingly complete and satisfactory collection of natural constants in a small bulk and a convenient form. It is unfortunate, but doubtless unavoidable, that the price has been fixed at nearly three times as much as that of the first edition.

ARTHUR B. LAMB.

**The Principles of the Phase Theory.** By DOUGLAS A. CLIBBENS, PH. D., Lecturer in Inorganic and Physical Chemistry in the University of London, King's College. Macmillan and Co., Limited. St. Martin's St., London, 1920. xx + 383 pages. 15 × 22.5 cm. Price \$10.00.

The title of this book, "The Principles of the Phase Theory" is misleading. Not only is there no discussion of the fundamental thermodynamic principles which underlie that portion of the study of heterogeneous equilibrium usually treated under the Phase Rule, but also there is no suggestion that there are such fundamental principles. The subtitle, "Heterogeneous Equilibrium between Salts and their Aqueous Solutions" is more truly descriptive, and the book will prove useful to those interested in this particular portion of the application of phase theory, and restricted to English texts.

The reviewer cannot agree with the author that "... a thorough study of the condensed system offers the easiest path to a true understanding of the methods of the Phase Theory," and believes that the reader who is unfamiliar with the subject, for whom the book is avowedly written, would have a clearer grasp of the equilibrium relations in systems in which hydrates are formed if the changes in pressure in the various univariant systems were coördinated with the changes in temperature and composition. The author frequently finds it necessary to disregard this limitation to condensed systems; for example, in order to explain the important process of isothermal evaporation. This process, as well as the relation of the condensed system to the isobaric saturation curve, would be understood more easily if a few isobars were included.

The chapters deal with condensed binary, ternary, quaternary and quinary systems, and the concluding chapter with graphical methods. The author does not have the gift of clear exposition, and devotes many pages to the detailed discussion of obvious geometrical relationships. The entire chapter on ternary systems is an example. It is hard reading, even for one familiar with, and interested in, the subject, and could be improved by elimination of much of the detailed discussion. The final chapter on graphical methods seems redundant. Its material either has been, or should have been, treated in preceding chapters, so that it becomes merely a further exercise in geometry. Indeed, to the reviewer it seems that this book carries to an extreme the too common tendency of writers on Phase

Rule to devote much space to geometry, without giving a hint as to the thermodynamical justification of the geometry. The paucity of literature references is surprising.

GEORGE W. MOREY.

**Allgemeine Photochemie. General Photochemistry.** By PROF. DR. phil. et chem. J. PLOTNIKOW, Director of the photochemical Research Laboratory at the Aktiengesellschaft für Anilinfabrikation Berlin-Treptow; o. Prof. and Direktor of the Chemischen Instituts at the former Kaiserlichen Universität at Moscow. Walter de Gruyter and Company, Berlin and Leipzig. 1920. 729 pp. 68 fig. 24 X 16 cm. Price \$7.00.

According to the preface of this book, the author, a Russian recently domiciled in Germany, began 10 years ago to write a complete encyclopedic handbook of photochemistry, but the political upheaval in Russia and his personal misfortunes prevented the full attainment of this end and he has had to be content with this volume of 700 odd pages, which in the subtitle he describes as a hand- and text-book, for the research, study and practice of photochemistry.

Irrespective of the book itself, this preface will command the interest and sympathy of future generations of students of photochemistry. It tells how the author, formerly Professor at and Director of, the Chemical Institute at the Imperial University of Moscow, began to write this book in the summer of 1917 on his country estate in the province of Riasau in Russia. The revolution started; day after day he saw the followers of Kerensky plunder and destroy the farm and estate to whose development he had devoted years of effort. His country library was destroyed in order to manufacture cigarettes! Then came the Bolshevik outbreak and he was obliged to flee to Moscow where only by selling his furniture and his scientific library, book by book, could he keep his family and himself from starvation. Finally even these means failed, and he and his family made their way to the Ukraine, but he was soon forced to flee from this refuge, at last reaching Germany in 1918, where he found assistance and relief among his scientific and industrial friends. During all this time he kept working on his book and succeeded in getting the manuscript safely to Germany and completing it there.

The book is divided into four parts. The first part, introductory in nature, discusses photochemical valence and the sensitivity of substances to light; states the fundamental laws of photochemistry, discussing the influence of temperature on the photochemical processes; classifies light reactions and gives a short tabular statement of the historical development of the subject.

The second part discusses the practice and theory of photochemical kinetics, catalysis and equilibria. The discussion of the practice or technique is brief, since this has been covered fully in the author's earlier

volume on that subject. The discussion of the mathematical theory is based largely on the author's independent development of his own theoretical views.

The third part, which constitutes the bulk of the book, is a detailed catalog and discussion of all the more important known photochemical reactions. Inorganic and organic reactions are discussed separately; those in the former group being classified according to the significant elements arranged in the order of the periodic system.

The fourth part of the book is devoted to the applications of photochemistry, chiefly photography of course, and this is by far the most sketchy and unsatisfactory part of the work.

The book as a whole will surely be of great usefulness to the students and investigators of photochemical subjects. It is impossible to form any judgment as to the permanent value of the theoretical treatment, but it cannot but be stimulating. The unified treatment of the whole subject, and the collection of photochemical reactions are certain to be valuable. The book suffers from too subjective a point of view. This is brought out perhaps too emphatically by the observation that in his tabulation of important events in the recent history of photochemistry only five entries since 1915 appear; they all refer to publications by the author, the present volume representing the culmination. Certain important aspects of the subject have also been given far too scanty attention. Thus the recent work of Marcelin and of W. C. M. Lewis is not mentioned; that of Perrin is dismissed with four lines of discussion.

Whoever reads the preface cannot, however, but view these blemishes with understanding and sympathy.

ARTHUR B. LAMB.

**Die Welt der vernachlässigten Dimensionen.** By WOLFGANG OSTWALD. Fifth and sixth editions. Theodor Steinkopff, Dresden and Leipzig, 1921. pp. xii + 253. 23 × 16 cm. Price 7 shillings.

The fourth edition was sold out in six months and we now have the fifth and sixth editions simultaneously, which seems a contradiction in terms. Merely as a matter of curiosity one would like to know how many editions can be issued simultaneously. Perhaps the author uses editions and thousands synonymously.

The author believes that this continued demand means that the book has become, or is going to become, an "Introduction to Colloid Chemistry." The reviewer does not quite see how a book which is in the form of lectures delivered in the winter of 1913-14 can be kept in that form and also up to date. The size of the book has increased 32 pages.

WILDER D. BANCROFT.

**Oedema and Nephritis.** A Critical, Experimental and Clinical Study of the Physiology and Pathology of Water Absorption in the Living Organism. By MARTIN H. FISCHER, M. D., Eichberg Professor of Physiology in the University of Cincinnati. Third and enlarged edition. John Wiley and Sons, Inc., New York; Chapman and Hall, Limited, London, 1921. xvi + 922 pp. 217 fig. 15.5 × 23.5 cm. Price \$10.00 (60s. net).

As the author informs us in the preface, he has left this third edition virtually unaltered in respect to every statement contained in the two preceding. He has, however, made a number of additions. These comprise a more detailed development of the concept of the hydrophilic colloid, observations on the swelling of aleuronat, further experiments on the swelling of gelatin in non-acid media, a discussion of the nature of the increase and decrease in hydration capacity of the proteins, a more extensive presentation of the author's conception of secretion, experimental evidence regarding the distinction between swelling and "solution" of colloids and on the behavior of proteins in the presence of buffer mixtures, renewed emphasis on the non-relationship, as the author holds, between disease of the kidney and the generally accepted signs, symptoms and complications of nephritis, additional suggestions regarding the treatment of nephritis, and an even more positive insistence upon the purely infectious origin of vascular disease and chronic interstitial nephritis.

In brief this book deals in very striking fashion with the bearings of colloid chemistry upon the problems of the relations of water to living matter. Its arrangement and printing are excellent, and its literary style clear, interesting and forcible, especially forcible for the author states his views with overwhelming positiveness. The polemical tone is doubtless in part at least a reaction to the acerbity with which some of Fischer's theoretical ideas were attacked and his practical deductions combated when first presented. But even his critics must concede that he was in many points essentially right, and that he was one of the first investigators to recognize the important part which, as nearly everyone now realizes, is played by the colloidal properties of living matter. Fischer may justly complain of the way in which certain methods of treatment (*e. g.*, sodium hydrogen carbonate for acidosis, and gum-saline after hemorrhage) which were criticized as unsound when presented by him some years ago have recently been brought forward by others without adequate credit to him who first suggested them. The reviewer once heard one of Fischer's critics state in a discussion before a scientific assembly that he, the critic, "refused to muddy his thoughts with colloids". Fischer has thrown much light upon a "muddy" field.

On the other hand, the tenacity with which Fischer defends every detail of any position which he has once taken must be admitted as a marked defect in this work. Even admitting that the author's own ideas were originally completely correct and may now be reprinted verbatim, it is

doubtful whether he himself would hold that the entire general background of information available in the literature when he first wrote was correct. Some of the work of others which he quoted as affording foundation and background for his own work must have been partly erroneous or now need re-interpretation. For example, it is highly probable now that the only acid which ever occurs free in any appreciable concentration in a living tissue is carbonic acid.

In the next edition of this work the leading rôle may well be taken with ever increasing confidence by colloids, but many of the conceptions which were generally prevalent, but vague or incorrect, a decade ago should now be discarded, and the author's own work should be presented against a background newer and more specific.

YANDELL HENDERSON.

**Lehrbuch der Cellulosechemie.** Für Studierende an technischen Hochschulen und Universitäten sowie für Cellulose-Fachleute. BY DR. EMIL HEUSER, a. o. Professor of Cellulosechemie at the Technischen Hochschule at Darmstadt. Gebrüder Borntraeger, Berlin, 1921. vii + 188 pp. 3 figs. 16.5 × 25.5 cm. Price M 32.

The volume, as stated in the introduction, has been written in response to a long felt need on the part of students of chemistry, paper-making, textile chemistry and related subjects, no book having hitherto been published on this subject. According to the author such a work should contain a brief, critical review of the important experimental facts and their bearing on the problem of the constitution of cellulose.

The difficulties surrounding the presentation of such a complex subject as cellulose chemistry have been satisfactorily overcome by a division of the subject under the six headings of (A) Alkali Cellulose, (B) Ester Formation, (C) Ether Formation, (D) Oxidation, (E) Decomposition Reactions, and (F) Constitution, each of which has been handled in a critical and illuminating manner. The treatise seems to be noticeably free from printer's errors. "Triglukose," p. 76, should evidently read "Trimethylglukose."

So marked is the present activity of scientific workers on the subject of the constitution of cellulose that the last chapter will probably stand in need of early revision.

The volume can be heartily recommended to all students of chemistry and especially to those interested in commercial progress in the field of cellulose products. No technical chemist can afford to disregard the scientific work at present being carried out in the various countries relating to the constitution of cellulose, for in the acquirement of this knowledge lies the surest road to new developments and progress in all branches.

HAROLD HIBBERT.





THE JOURNAL  
OF THE  
American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL  
INSTITUTE OF COPENHAGEN.]

STUDIES ON SOLUBILITY. III. THE SOLUBILITY OF METAL  
AMMONIA SALTS IN SALT SOLUTIONS.

By J. N. BRÖNSTED AND AGNES PETERSEN.

Received April 4, 1921.

Introduction.

In two previous papers<sup>1,2</sup> one of the writers has given views on the treatment of solubility equilibria, involved when salt solutions are employed as solvents for salts. To illustrate the scope of these views a few results were communicated from an extensive series of experimental determinations on solubility, dealing mainly with solubility of metal ammonia salts in solutions of other salts. In this and later articles a more complete statement of the data procured and of additional experiments will be given.

The employment of metal ammonia salts is specially fitting for the purpose of studying the laws of solubility. They are in general really strong electrolytes, and for the most part not liable to hydrolysis of any kind. On account of the great number of cations and anions belonging to this group the number of salts it contains is extremely high. The solubility is usually small, and salts of a solubility between 0.01 and 0.0001 molal,

<sup>1</sup> Brönsted, *THIS JOURNAL*, 42, 761 (1920).

<sup>2</sup> *Ibid.*, 42, 1448 (1920).

the most convenient range of concentration for the theoretical and experimental treatment, can be prepared easily, abundantly and usually in a very pure state. Finally, and this point is not to be undervalued, the determinations of solubility can for all compounds of this type be carried out uniformly, namely by decomposing with alkali, with or without addition of reducing substances such as stannous chloride, by simply estimating the ammonia liberated by adsorption in sulfuric acid, using methyl red as an indicator.

A number of the salts employed for our investigations have been described before in the publications of the leading authors in this domain, S. M. Jørgensen and A. Werner. A good many, however, have been produced for the first time by us. As in all such cases the constituent ions were well known, we have confined ourselves to an analysis of their ammonia and water contents. In order to secure the high purity which was essential, the whole sample of each salt was stirred repeatedly with fresh portions of water till a constant solubility was found. The salt was considered pure when this constant value agreed with that found when using only a small quantity of salt for solution.

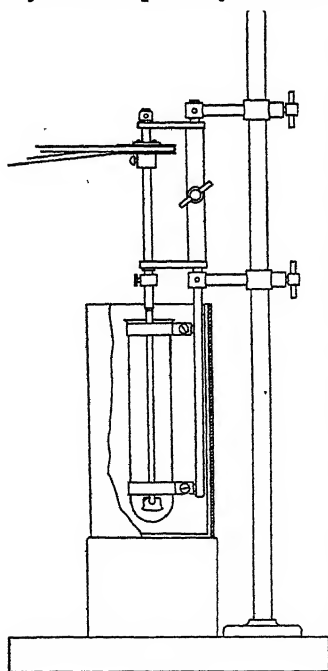


Fig. 1.

The temperatures of the experiments were  $0^{\circ}$  and  $20^{\circ}$ . Determinations were made on a number of salts at both temperatures, whereby the important figures for the temperature coefficient, to be considered later, have been obtained. The praseo salts are the most unstable within the range of compounds employed and could not be studied at  $20^{\circ}$ ; but other salts are also transformed in solution and so give solubility values, which slowly increase with the time, especially at  $20^{\circ}$ . As the velocity of solution for a metal ammonia salt is generally rather high such slow transformations were usually no hindrance in our determinations.

The determinations at  $20^{\circ}$  were carried out in an ordinary thermostat, regulating to within  $\pm 0.01^{\circ}$ . The apparatus employed for the measurements at  $0^{\circ}$  is shown in Fig. 1. When saturation had taken place a known volume of the saturated solution was sucked out through a small cotton plug, and the determination of the concentration made as described above.

In judging the accuracy reached by our measurements we must distinguish between relative and absolute exactness. When a series of ex-

periments is carried out with the same sample of salt using the same acid for estimation and working under the best conditions obtainable, the possible relative error in the determinations will hardly reach some tenths of a per cent., and the possible absolute error 1%. Especially in that part of our data which was first obtained and most of which appears in the first part of the tables following the accuracy is probably considerably lower.

In carrying out these determinations we were valuably assisted by cand. polyt. Max Möller, and cand. polyt. E. Smith-Jensen to whom the writers wish to express their best thanks. We likewise wish to express our indebtedness to Carlsbergfonden for subsidizing the work.

### I. Solubility of Metal Ammonia Salts in Water.

We shall first give a survey of the metal ammonia ions, and others, constituting the salts employed in our determination. The names, formulas and valences of the ions used, are given below.

Ion.	Formula and Valence.
Luteo cobaltic or hexammine cobaltic.....	$[\text{Co}(\text{NH}_3)_6]^{+++}$
Roseo cobaltic or aquo-pentammine cobaltic.....	$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{+++}$
Tri-ethylene-diamine cobaltic.....	$[\text{Co}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]^{+++}$
Chloro-pentammine cobaltic.....	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$
Chloro-pentammine chromic.....	$[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{++}$
Chloro-pentammine rhodium.....	$[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{++}$
Chloro-aquo-tetrammine cobaltic.....	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{++}$
Bromo-pentammine cobaltic.....	$[\text{Co}(\text{NH}_3)_5\text{Br}]^{++}$
Xantho cobaltic or nitro-pentammine cobaltic.....	$[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$
Thiocyanato-pentammine cobaltic.....	$[\text{Co}(\text{NH}_3)_5\text{CNS}]^{++}$
Praseo cobaltic or dichloro-tetrammine cobaltic....	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
Croceo cobaltic or dinitro-tetrammine cobaltic (trans)	$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$
Flavo cobaltic or dinitro-tetrammine cobaltic (cis)...	$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$
Oxalo-tetrammine cobaltic.....	$[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$
Carbonato-tetrammine cobaltic.....	$[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$
Sulfato-pentammine cobaltic.....	$[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$
Tetranitro-diammine cobaltiate.....	$[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$
Tetrathiocyanato-diammine chromiate.....	$[\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]^-$
Oxalo-dinitro-diammine cobaltiate.....	$[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{O}_4)(\text{NO}_2)_2]^-$
Dioxalo-diammine cobaltiate.....	$[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2]^-$
Dioxalo-triammine cobaltiate.....	$[\text{Co}(\text{NH}_3)_3(\text{C}_2\text{O}_4)_2]^-$
Hexathiocyanato chromiate.....	$[\text{Cr}(\text{CNS})_6]^{---}$
Hexacyano ferriate.....	$[\text{Fe}(\text{CN})_6]^{---}$
Hexacyano cobaltiate.....	$[\text{Co}(\text{CN})_6]^{---}$
Trioxalo cobaltiate.....	$[\text{Co}(\text{C}_2\text{O}_4)_3]^{---}$

The following table records the solubilities of salts formed by these and more usual cations and anions, using pure water as solvent.

In all cases when not otherwise especially indicated, the figures for solubilities and concentrations mean molal concentrations; for luteo sulfate, for example, the number of molecules of  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$  in one liter of the solution. The abscissas of the figures are in equivalents of added salt per liter.

TABLE I.—SOLUBILITY OF METAL AMMONIA SALTS IN WATER.

## I. Salts Containing a Univalent Cation.

	0°.	20°.	$S_{20^{\circ}}/S_{0^{\circ}}$ .
Cesium tetranitro-diammine cobaltiate.....	0.00531	0.01720	3.24
Cesium tetrathiocyanato-diammine chromiate.....	0.000790	0.00258	3.26
Potassium tetranitro-diammine cobaltiate.....	0.0240		
Silver tetranitro-diammine cobaltiate.....	0.000772	0.00210	2.72
Silver oxalo-dinitro-diammine cobaltiate.....	0.00278	0.00822	2.96
Thallous tetranitro-diammine cobaltiate.....	0.00251	0.00789	3.14
Thallous oxalo-dinitro-diammine cobaltiate.....	0.00420	0.00977	2.34
Tetramethylammonium-tetranitro-diammine cobaltiate.	0.00749	0.0197	2.63
Carbonato-tetrammine-cobaltic-tetrathiocyanato cobaltic sulfate.....		0.07	
Carbonato-tetrammine-cobaltic-tetrathiocyanato cobaltic chromiate, $\beta$ .....	0.00185	0.00555	3.00
Carbonato-tetrammine-cobaltic-tetranitro-diammine cobaltiate.....	0.00366	0.0124	3.42
Croceo bromide.....	0.012		
chloride.....	0.0222	0.043	1.95
dioxalo-diammine cobaltiate.....	0.000066		
dioxalo-triammine cobaltiate.....	0.00059		
hexachloro-platinate.....	0.00233		
nitrate, $\alpha$ .....	0.00546	0.01483	2.71
nitrate, $\beta$ .....	0.00494	0.01298	2.62
perchlorate.....	0.0124	0.0290	2.34
picrate $\beta$ .....		0.00704	
selenate.....		0.0092	
sulfate.....	0.00096	0.00411	4.17
tetrachloro-aurate.....		0.017	
tetranitro-diammine cobaltiate.....	0.000096	0.000355	3.70
tetrathiocyanato-diammine chromiate.....	0.000057	0.000143	3.11
Flavo tetranitro-diammine cobaltiate.....	0.000949	0.0033	3.46
tetrathiocyanato-diammine chromiate, $\alpha$ .....	0.000322	0.00100	3.11
tetrathiocyanato-diammine chromiate, $\beta$ .....		0.00073	
chloride.....		0.034	
Oxalo-tetrammine-cobaltic hexathiocyanato chromiate..	0.00053		
nitrate.....	0.0066	0.018	2.73
perchlorate.....	0.0051	0.0140	2.74
tetranitro-diammine cobaltiate.....	0.00103		
trioxalo cobaltiate.....	0.00083		
Praseo bromide.....	0.00632		
chlorate.....	0.0180		
chloride.....	0.0141		
dioxalo-diammine cobaltiate.....	0.000171		
hexacyano ferriate.....	0.000121		
iodate.....	0.00441		

nitrate.....	0.00383		
picrate.....	0.00021		
thiocyanate.....	0.00289		
Sulfato-pentammine cobaltic nitrate.....		0.026	

## II. Salts Containing a Bivalent Cation.

	0°.	20°.	$S_{20^{\circ}}/S_{0^{\circ}}$ .
Magnesium dinitro-oxalo-diammine cobaltate.....	0.00348		
Bromo-pentammine cobaltic bromide.....	0.00275		
chloride.....	0.00542	0.011	2.0
nitrate.....	0.0	0.010	
Bromo-pentammine rhodium chloride.....		0.015	
Chloro-aquo-tetrammine cobaltic chloride.....	0.057	0.11	1.9
Chloro-pentammine chromium.....	0.000660		
Chloro-pentammine chromium chloride.....	0.0149	0.030	2.0
nitrate.....		0.055	
oxalate.....	0.00125		
cobaltic bromide.....	0.00725		
chloride.....	0.00914	0.018	2.0
iodate.....	0.00200		
hexachloro-platinate.....	0.000091		
nitrate.....		0.046	
oxalate.....	0.00036		
sulfate.....		0.029	
tetranitro-cobaltate.....	0.0001731	0.000637	3.1
rhodium chloride.....	0.00945	0.020	2.1
Thiocyanato-pentammine chromium chloride.....		0.040	
cobaltic chloride.....		0.039	
chromate.....	0.00107		
iodate.....		0.00505	
sulfate.....		0.0290	
Xantho chloride.....		0.11	
chromate.....	0.000258	0.000547	2.12
nitrate.....	0.0170	0.038	2.2
oxalate.....	0.000161	0.000432	2.68
tetranitro-diammine cobaltate.....	0.00031	0.00099	3.2
tetrathiocyanato-diammine chromate.....	0.000392	0.001284	3.27

## III. Salts Containing a Trivalent Cation.

	0°.	20°.	$S_{20^{\circ}}/S_{0^{\circ}}$ .
Luteo cobaltic chloride.....		0.26	
chloride sulfate.....	0.01055		
hexacyano chromiate.....	0.000028		
cobaltate.....	0.000007	0.000016	2.3
ferriate.....	0.000009	0.000022	2.4
iodate.....	0.00181	0.00458	2.53
nitrate.....	0.0202	0.052	2.6
sulfate.....	0.0090	0.020	2.2
tetranitro cobaltate.....	0.000043		
trioxalo cobaltate.....	0.000019		
Roseo cobaltic hexacyano ferriate.....	0.000172		
sulfate.....		0.016	
tetrathiocyanato-diammine chromiate..	0.00006		

## II. Uni-univalent Salts in Uni-univalent Solvents.

With most of the uni-univalent salts specified in the foregoing section, determinations have been carried out using as solvents salt solutions of various concentrations. In a previous paper the following equation was found to indicate the change in solubility with the concentration, based

$$\log \frac{s}{s_0} = a(\sqrt[3]{c_i} - \sqrt[3]{s_0})$$

on the assumption of Noyes and Falk<sup>3</sup> of the equality of the activity coefficients and the validity of the expression for the lowering of the freezing point.

The experimental results are given in the following tables. The value of the coefficient  $a$ , which may be calculated according to the above equation for each concentration of the solvent  $c = c_i - s$  is also given in the tables to show the validity of the underlying assumptions.

The first data are those of certain praseo cobaltic salts. As mentioned above, the praseo salts are rather unstable in aqueous solutions, owing to the progress of the reaction



easily observable through the change in color of the solution from green to red. This reaction takes place rapidly at 20°, and constant figures are therefore not to be obtained at this temperature. At 0°, when the time of stirring varies, no appreciable change in solubility is observed within 5 to 10 minutes. As the salts dissolve very quickly, reliable results can be obtained at this temperature. The figures at least will be mutually comparable even when the absolute values may be somewhat more uncertain here than in most other cases.

TABLE II.—PRASEO THIOCYANATE.  $(\text{Co}(\text{NH}_3)_4\text{Cl}_2)\text{CNS}$ .  $s_0 = 0.00289$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .	Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KOOCH	0.01	300	1.038	(0.175)	NaCl	0.02	313	1.108	0.309
	0.03	321	1.111	0.255		0.05	332	1.173	0.295
	0.05	331	1.146	0.252		0.1	353	1.247	0.292
	0.1	345	1.194	0.235					0.30
	0.2	374	1.294	(0.251)	KClO <sub>3</sub>	0.02	318	1.124	0.353
	0.5	409	1.415	(0.231)		0.05	339	1.198	0.333
	1.0	439	1.519	(0.211)		0.1	365	1.288	0.335
				0.25					0.34
KCl	0.02	314	1.110	0.314	NaClO <sub>3</sub>	0.02	316	1.115	0.329
	0.05	336	1.187	0.317		0.05	337	1.191	0.323
	0.1	358	1.265	0.311		0.1	361	1.274	0.320
	0.2	389	1.375	0.313					0.32
				0.31					

<sup>3</sup> Noyes and Falk, *THIS JOURNAL*, 32, 1011 (1910); 33, 1436 (1911); 34, 454, 458 (1912).

For the calculation of  $s/s_0$  in the last four solvents the value  $s_0 = 0.00283$  was used as found in this series of experiments. The value of  $a$  for sodium chlorate becomes a little greater than that given in the previous paper (0.30).

TABLE III.—PRASEO NITRATE.  $(\text{Co}(\text{NH}_3)_4\text{Cl}_2)\text{NO}_3$ .  $s_0 = 0.00383$ .

Solvent.	$c$ .	$s \times 10^3$ .	$s/s_0$ .	$a$ .	Solvent.	$c$ .	$s \times 10^3$ .	$s/s_0$ .	$a$ .
KOOCH	0.005	395	1.031	(0.262)	NaCl	0.005	395	1.032	(0.262)
	0.01	409	1.068	0.335		0.01	405	1.057	0.286
	0.05	455	1.188	0.336		0.05	449	1.173	0.310
	0.1	487	1.272	0.331		0.1	480	1.253	0.311
	0.2	533	1.392	(0.331)					0.30
	0.5	635	1.658	(0.343)	HCl	0.005	404	1.055	(0.447)
	1.0	760	1.984	(0.352)		0.01	410	1.070	0.348
				0.33		0.05	447	1.167	0.301
						0.1	474	1.238	0.294
KCl	0.005	399	1.042	0.345					0.31
	0.01	408	1.065	0.323					
	0.03	434	1.133	0.322					
	0.05	458	1.196	0.349	NaC <sub>6</sub> H <sub>5</sub> SO <sub>3</sub>	0.005	394	1.029	(0.241)
	0.1	496	1.295	0.356		0.01	404	1.055	0.274
				0.34		0.05	445	1.162	0.293
						0.1	477	1.245	0.303
						0.2	519	1.355	0.305
									0.29

Experiments were also made with praseo nitrate in potassium and sodium chlorate solutions, but the increase in solubility is here much smaller than in the case of other solvents. Moreover the values were found to decrease with increasing time of stirring. Some special reaction must here evidently take place.

Inspection of the data in Tables II and III shows that the solubility of the two salts concerned increases with increasing concentration of the solvent, in all cases in close analogy to what has been stated in the previous article. The values of  $a$  for any solvent show a marked agreement and approximation to the value  $1/3$ . For the calculation of the mean of the values of  $a$ , the solutions stronger than 0.1 molal, for which the solubility equation at any rate does not hold good, and the most diluted ones, in which the experimental error has too great influence, have been excluded. In these and subsequent tables  $t = 0^\circ$ , except when otherwise indicated.

With praseo bromide in addition to salt solutions both acetic acid and the three-chloro-acetic acids have been used. The incomplete dissociation of these acids is very markedly proved in the values of  $s/s_0$  and  $a$ . While for all salt solvents the calculated normal values of  $a$  are in the neighborhood of 0.3, using these acids we find that increasing concentration is accompanied by a rapid decrease in this coefficient. This phenomenon is extremely pronounced with the weak acetic acid, but also the substituted

acid and even the trisubstituted acid show similar behavior. This indicates that not even trichloro-acetic acid is a really strong electrolyte.

TABLE IV.—PRASEO IODATE.  $(\text{Co}(\text{NH}_3)_4\text{Cl}_2)\text{IO}_3$ .

$s_0 = 0.00441$ .				
Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KCl	0.02	487	1.104	0.337
	0.05	525	1.191	0.349
	0.1	571	1.295	0.363
				0.35
NaCl	0.02	486	1.102	0.330
	0.05	524	1.188	0.345
	0.1	568	1.288	0.356
				0.34
$\text{KClO}_3$	0.02	491	1.113	0.364
	0.05	531	1.204	0.372
	0.1	579	1.313	0.383
				0.37
$\text{NaClO}_3$	0.02	491	1.113	0.364
	0.05	528	1.197	0.360
	0.1	576	1.306	0.375
				0.37

TABLE V.—PRASEO PICRATE.

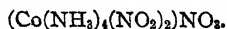
$(\text{Co}(\text{NH}_3)_4\text{Cl}_2)\text{C}_6\text{H}_5\text{N}_2\text{O}_7$ .				
$s_0 = 0.000212$ .				
Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KCl	0.02	25.7	1.215	0.396
	0.05	27.4	1.292	0.360
	0.1	29.5	1.392	0.354
	0.2	33.5	1.580	(0.378)
	0.5	41.8	1.972	(0.401)
	1.0	53.6	2.528	(0.428)
				0.37
NaCl	0.02	25.3	1.193	0.360
	0.05	26.6	1.255	0.318
	0.1	28.5	1.347	0.319
	0.2	30.1	1.420	(0.290)
	0.5	33.8	1.594	(0.274)
	1.0	41.4	1.953	(0.309)
				0.33

TABLE VI.—PRASEO BROMIDE.  $(\text{Co}(\text{NH}_3)_4\text{Cl}_2)\text{Br}$ .  $s_0 = 0.00632$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .	Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KOOCH	0.02	678	1.073	0.267	$\text{CCl}_3\text{COOH}$	0.02	681	1.078	0.283
	0.05	720	1.139	0.283		0.05	703	1.112	0.231
	0.1	752	1.190	0.260		0.1	731	1.157	0.218
	0.2	805	1.274	(0.258)		0.2	752	1.190	0.186
				0.27					
$\text{KOCCCCl}_2$	0.02	683	1.081	0.294	$\text{CHCl}_2\text{COOH}$	0.02	677	1.071	0.261
	0.05	719	1.138	0.279		0.05	702	1.111	0.228
	0.1	755	1.185	0.266		0.1	723	1.144	0.201
	0.2	802	1.269	(0.254)		0.2	740	1.171	0.168
				0.28					
$\text{KOCCCHCl}_2$	0.02	689	1.090	0.327	$\text{CH}_2\text{ClCOOH}$	0.02	656	1.038	0.143
	0.05	725	1.147	0.297		0.05	673	1.065	0.137
	0.1	763	1.207	0.281		0.1	677	1.071	0.103
	0.2	811	1.283	(0.266)		0.2	685	1.084	0.086
				0.30					
$\text{KOCCCH}_2\text{Cl}$	0.02	687	1.087	0.316	$\text{CH}_3\text{COOH}$	0.02	638	1.010	0.036
	0.05	726	1.149	0.300		0.05	642	1.016	0.034
	0.1	764	1.209	0.283		0.1	641	1.014	0.021
	0.2	818	1.295	0.275		0.2	636	1.006	0.007
				0.29					



The croceo cobaltic salts are rather stable in solution and give as a rule easily reproducible values for their solubilities. Some of the figures for croceo nitrate stated below have been communicated in an earlier paper,<sup>4</sup> where the existence of two modifications, an  $\alpha$ - (unstable) and a  $\beta$ -modification (stable), was indicated.

TABLE VII.— $\beta$ -CROCEO NITRATE.

$s_0 = 0.00494$ .				
Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KOOCH	0.02	536	1.086	0.290
	0.05	575	1.164	0.311
	0.1	621	1.258	0.328
	0.2	693	1.404	0.350
				0.32
KSCN	0.02	546	1.107	0.355
	0.05	596	1.208	0.387
	0.1	663	1.344	0.422
				0.38
KOH	0.02	553	1.120	
	0.05	405	0.820	
	0.1	311	0.630	

TABLE VIII.— $\beta$ -CROCEO NITRATE.

$t = 20^\circ$ . $s_0 = 0.01298$ .				
Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KOOCH	0.05	1467	1.130	0.320
	0.1	1570	1.210	0.329
	0.2	1713	1.320	(0.329)
	0.5	2035	1.568	(0.343)
				0.32
$\text{CCl}_3\text{COOH}$	0.2	1547	1.190	(0.207)
	0.387	1601	1.234	(0.181)

We find again constant values for  $a$  when potassium formate is used as a solvent, while potassium thiocyanate gives increasing values. Special attention should be called to the behavior of potassium hydroxide as solvent. We find here an increase in the solubility only with the most diluted solution. At higher concentrations it falls very markedly, indicating a specific effect of the solvent. To explain the phenomenon we imagined the possibility of a separation of croceo hydroxide in the solid state. On adding a solution of molal sodium hydroxide to a solution of croceo nitrate or croceo chloride, we indeed observed the appearance of a crystalline precipitation of a sparingly soluble compound. This proved, however, to be croceo carbonate, and does not appear when using pure solutions. As solubility measurements are carried out with an hydroxide entirely free from carbon dioxide, the explanation of the phenomenon is not to be found here. It may be due to a special reaction between the solvent and the saturating salt, or it may be looked upon as a peculiarity of the solvent, manifesting itself through an exceedingly great "salting out" effect. Of course, merely using this expression does not explain the phenomenon. However, it is sufficient to place it in that great field of phenomena which are of deep significance in connection with the theory of solubility and with which we will deal more thoroughly in subsequent articles.

<sup>4</sup> *Meddel. K. Vetenskapsakad. Nobelinstit.,* 5, 25 (1919).

When using potassium and sodium chloride solutions as solvents, other peculiarities were noted. The increase in solubility of croceo nitrate is found to be much less than otherwise, for example with 0.1 *N* solutions at 0° for potassium chloride, 1.16; and for sodium chloride, 1.14. This phenomenon was also studied by using mixed nitrate and chloride solutions as solvent and will be discussed more thoroughly when the question of such mixed solvents is taken up.

TABLE IX.—CROCEO TETRANITRO-DIAMMINE COBALTIATE.  $(\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2)(\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4)$ .

Solvent.	$s_0 = 0.000096.$			
	<i>c.</i>	$s \times 10^3.$	$s/s_0.$	<i>a.</i>
KOOCH	0.05	11.9	1.24	0.287
	0.1	12.8	1.33	0.297
	0.2	13.9	1.45	(0.249)
	0.5	17.5	1.82	(0.346)
				0.29
KCl	0.05	12.4	1.29	0.341
	0.1	13.2	1.38	0.332
	0.2	14.9	1.55	(0.354)
	0.5	20.2	2.10	(0.431)
				0.34

TABLE XI.—CROCEO DIOXALO-TRIAMMINE COBALTIATE.  $(\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2)(\text{Co}(\text{NH}_3)_3(\text{C}_2\text{O}_4)_2)$ .

Solvent.	$s_0 = 0.000593.$			
	<i>c.</i>	$s \times 10^3.$	$s/s_0.$	<i>a.</i>
KOOCH	0.1	89.5	1.509	0.468
	1.0	233	3.93	(0.648)
				0.47
KCl	0.02	70.3	1.186	0.388
	0.05	79.0	1.332	0.435
	0.1	91.7	1.546	0.496
	1.0	334	5.633	(0.818)
				0.44

TABLE X.—CROCEO PERCHLORATE.  $(\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2)\text{ClO}_4$ .

Solvent.	$s_0 = 0.01239.$			
	<i>c.</i>	$s \times 10^3.$	$s/s_0.$	<i>a.</i>
KOOCH	0.05	1423	1.148	0.356
	0.1	1566	1.264	0.398
				0.38
NaOOCH	0.05	1362	1.099	0.246
	0.1	1420	1.146	0.233
				0.24
KOCCCCl <sub>2</sub>	0.1	1562	1.261	0.393
				0.39
CCl <sub>3</sub> COOH	0.1	1398	1.128	0.207

TABLE XII.—CROCEO CHLORIDE.  $(\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2)\text{Cl}$

Solvent.	$s_0 = 0.0222.$			
	<i>c.</i>	$s \times 10^3.$	$s/s_0.$	<i>a.</i>
KOOCH	0.02	2310	1.043	0.261
	0.05	2400	1.084	0.252
	0.1	2520	1.136	0.253
				0.26

TABLE XIII.—OXALO-TETRAMMINE COBALTIC NITRATE.  $(\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4)\text{NO}_3$ .  $s_0 = 0.00658.$

Solvent.	<i>c.</i>	$s \times 10^3.$	$s/s_0.$	<i>a.</i>
KCl	0.02	736	1.119	0.429
	0.05	803	1.220	0.433
	0.1	905	1.375	0.477
				0.43

The figures in Tables IX, X and XI show values of *a* which are rather variable when the concentration changes. This is especially noteworthy

in the instance of the dioxalo-triammine cobaltiate. The rise in solubility is here much greater than usual.

In Table XII are given the figures obtained with croceo chloride, the most soluble of the croceo salts employed.

Further measurements were carried out with oxalo-tetrammine cobaltic salts. These are stable in solution, but it is more difficult to produce them in a quite pure state than the croceo salts. The data given in Tables XIII, XIV, XV and XVI will therefore scarcely possess the same degree of accuracy.

TABLE XIV.—OXALO-TETRAMMINE  
COBALTIC TETRANITRO-DIAMMINE  
COBALTIATE.  $(\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4)\text{-}$   
 $(\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4)$ .

Solvent.	$s_0 = 0.00103.$			
	<i>c.</i>	$s \times 10^4.$	$s/s_0.$	<i>a.</i>
KOOCH	0.02	112	1.09	0.214
	0.05	121	1.18	0.261
	0.1	132	1.28	0.297
				0.26
NaOOCH	0.02	111	1.08	0.194
	0.05	120	1.17	0.245
	0.1	128	1.25	0.265
				0.24
KCl	0.02	115	1.12	0.275
	0.05	123	1.20	0.291
	0.1	137	1.33	0.340
				0.30
NaCl	0.02	114.5	1.12	0.27
	0.05	123	1.20	0.290
	0.1	137	1.33	0.339
				0.30
KNO <sub>3</sub>	0.02	116	1.13	0.297
	0.05	126	1.22	0.324
	0.1	141	1.37	0.373
				0.33

TABLE XV.—OXALO-TETRAMMINE COBAL-  
TIC PERCHLORATE.  $(\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4)\text{ClO}_4.$

Solvent.	$s_0 = 0.00508.$			
	<i>c.</i>	$s \times 10^4.$	$s/s_0.$	<i>a.</i>
KOOCH	0.05	616	1.21	0.395
	0.1	679	1.34	0.417
	0.2	796	1.57	(0.464)
				0.40
NaOOCH	0.05	596	1.17	0.330
	0.1	640	1.26	0.332
	0.2	718	1.41	(0.357)
				0.33
KCl	0.05	634	1.25	0.456
	0.1	712	1.40	0.484
				0.47
NaCl	0.05	614	1.21	0.388
	0.1	684	1.35	0.426
				0.41
KOOCCCl <sub>3</sub>	0.1	677	1.33	0.44
	0.2	781	1.54	(0.444)
				0.44
CCl <sub>3</sub> COOH	0.1	607	1.11	0.256
	0.2	638	1.26	(0.236)
				0.26

Thallous tetranitro-diammine cobaltiate, with which salt a series of measurements was also carried out, showed surprisingly small increases in the solubility, as indicated in Table XVII. The small solubilities in potassium salt solutions are probably due to the formation of a solid mixture of thallous and potassium tetranitro-diammine cobaltiate.

TABLE XVI.—OXALO-TETRAMMINE COBALTIC PERCHLORATE.  $t = 20^\circ$ .  $s_0 = 0.0140$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KOH	0.02	1603	1.143	0.652
	0.05	1814	1.287	0.670
	0.1	1808	1.290	0.443

TABLE XVII.—THALLOUS TETRANITRO-DIAMMINE COBALTIATE.  $(\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4)\text{Cl}$ .

$$s_0 = 0.00259.$$

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .	Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	$a$ .
KOOCH	0.02	273	1.053	0.153	KClO <sub>3</sub>	0.02	274	1.055	0.159
	0.05	285	1.097	0.169		0.05	287	1.108	0.188
	0.1	287	1.108	0.135		0.1	298	1.150	0.184
	0.15	283	1.093	0.095					0.18
	0.2	277	1.067	0.063					
					KNO <sub>3</sub>	0.02	278	1.072	0.206
						0.05	294	1.134	0.230
						0.1	308	1.187	0.224
									0.22

In the following table are collected all the  $a$  values found with various solutes and solvents according to the preceding figures given above.

TABLE XVIII.—THE  $a$  VALUES AT  $0^\circ$ .

Solvent. →	KOOCH.	NaOOCH.	KCl.	NaCl.	KNO <sub>3</sub> .	KClO <sub>3</sub> .	NaClO <sub>3</sub> .	KOCCCl <sub>3</sub> .	KSCN.	NaSO <sub>4</sub> C <sub>6</sub> H <sub>5</sub> .	HCl.
Salt.											
Praseo thiocyanate....	0.25		0.31	0.30		0.34	0.32				
nitrate.....	0.33		0.34	0.30						0.29	0.31
iodate.....			0.35	0.34		0.37	0.37				
picrate.....			0.37	0.33							
bromide.....	0.27							0.28			
Croceo nitrate.....	0.32								0.38		
tetranitro co-											
baltiate.....	0.29		0.34								
perchlorate....	0.38	0.24							0.39		
oxalo-triammine											
cobaltiate....	0.47										
chloride.....	0.26										
Oxalo-tetrammine [co-											
baltic nitrate...			0.43								
tetranitro co-											
baltiate.....	0.26	0.24	0.30	0.30	0.33						
perchlorate....	0.40	0.33	0.47	0.41				0.41			

The mean value of all these figures is  $a = 0.31$ , which is in accordance with the  $a$ -value derived from the freezing-point measurements as shown in the previous paper. Inspection of Table XVIII and the foregoing tables shows, however, that we cannot count upon constant  $a$  values, even if one salt is considered in connection with different solvents, or what was

more probable, when one solvent is considered in connection with different salts. There is, however, an important regularity to which attention must be called. When a solvent proves of greater dissolving power in one instance, it seems to prove so in all. We see, for example, that potassium salts have a greater dissolving effect than sodium salts, chlorates than chlorides, and these again than formates, etc. With a single exception, that of praseo nitrate in potassium formate solution, the sequence of solvent power for all of the salts for which sufficient data have been procured, is as follows: potassium chlorate, sodium chlorate, potassium chloride, sodium chloride, potassium formate, sodium formate.

This sequence is observed not only with uni-univalent salts, with which we are dealing, but also with salts of other types, and especially when non-electrolytes are considered. We shall in a later paper deal more in detail with this fact, which is of high importance for our conception of electrolytic solution. The sequence also, as far as reliable data are available, is coincident with that obtained by ranging the salts according to their freezing-point lowering. Of all salts employed, potassium nitrate showed the slightest lowering of the freezing point and at the same time produced the greatest increase in solubility. From both of these facts we infer that the activity coefficients of univalent ions have smaller values here than in the other solvents employed. Sodium formate on the other hand shows large values for the freezing-point lowering and correspondingly less solvent power than the other salts. At any rate these are phenomena to be duly regarded as derived from a rigid relation between osmotic and activity properties of solutions.

It cannot, however, be denied, that really constant  $\alpha$  values are not obtained in most cases, even with very sparingly soluble salts. We can imagine that the incompleteness of our hypothesis is the reason for such deviations. It is true that the secondary electric effect spoken of in the previous paper may influence the activity to a considerable extent, even with univalent ions. On the other hand the cube root expression of Noyes and Falk,<sup>3</sup> underlying our calculation of the  $\alpha$  values, certainly gives no exact representation of the freezing-point curves, as illustrated in a recent publication of G. N. Lewis and G. A. Linhart,<sup>5</sup> and many discrepancies may be due to this fact.

The equation found by Lewis and Linhart, claimed by them to be of universal validity, is

$$\log \left( n\lambda - \frac{\theta}{c} \right) = \alpha \log c + \log \beta, \quad (1)$$

where  $n$  is the number of ions formed by one mol of salt on complete dissociation,  $\lambda$  the theoretical molecular freezing-point lowering (1.858°),  $\theta$

<sup>5</sup> Lewis and Linhart, *THIS JOURNAL*, **41**, 1951 (1919).

the lowering found,  $c$  the concentration and  $\alpha$  and  $\beta$  constants. The equation may also be written,

$$\Delta = \Delta_0 - \beta c^\alpha, \quad (2)$$

where  $\Delta$  and  $\Delta_0$  indicate the molal lowering observed and calculated, respectively.

In the first two columns of Table XIX are given the values of  $\alpha$  and  $\beta$  for a number of salts calculated by Lewis.

TABLE XIX.

	$\alpha$ .	$\beta$ .		$\alpha$ .	$\beta$ .
KCl	0.535	1.223	K <sub>2</sub> SO <sub>4</sub>	0.374	3.187
NaCl	0.535	1.223	BaCl <sub>2</sub>	0.364	2.660
KIO <sub>3</sub>	0.442	1.196	CoCl <sub>2</sub>	0.362	2.456
NaIO <sub>3</sub>	0.442	1.196	Mean	0.37	2.7
Mean	0.49	1.21	MgSO <sub>4</sub>	0.293	3.404
			CdSO <sub>4</sub>	0.325	4.421
			Mean	0.31	3.9

In the last two columns we have added the mean values of  $\alpha$  and  $\beta$ . According to these figures it seems that the  $\alpha$ -values decrease, and the  $\beta$ -values increase, by increasing valences of the ions.

The term  $\gamma = \frac{x}{c}$ , called by Lewis the thermodynamic or corrected degree of dissociation, is the same as the activity coefficient  $f$  used throughout the previously mentioned papers. Equation 17 in Lewis' paper expressing the relationship between activity coefficient and concentration is easily reached by introducing the osmotic coefficient,

$$\varphi = \frac{\Delta}{\Delta_0}, \quad (3)$$

and the relation between this and the activity coefficient,

$$c \frac{d \ln f}{dc} = c \frac{d\varphi}{dc} - (1 - \varphi). \quad (4)$$

Substituting here from Equation 2

$$\varphi = 1 - \frac{\beta c^\alpha}{\Delta_0}$$

and hence,

$$\frac{d\varphi}{dc} = -\frac{\beta}{\Delta_0} \alpha c^{\alpha-1}$$

We then find,

$$\ln f = -\frac{\beta(1+\alpha)}{\Delta_0 \alpha} \cdot c^\alpha \quad (5)$$

which is identical with Equation 17 of Lewis and Linhart.

In the case of saturation of a binary salt in a binary hetero-ionic solvent we have, when  $s$  indicates the solubility,

$$sf = \text{Const.}$$

or

$$\log s = \frac{\beta(1 + \alpha) c^\alpha}{2.303 \Delta_0 \alpha} + \text{const.} \quad (6)$$

Introducing for the solubility in pure water,

$$\log s_0 = \frac{\beta(1 + \alpha) s_0^\alpha}{2.303 \Delta_0 \alpha} + \text{const.,}$$

and putting

$$\frac{\beta(1 + \alpha)}{2.303 \Delta_0 \alpha} = L \quad (7)$$

we obtain

$$\log \frac{s}{s_0} = L \cdot c^\alpha \quad (8)$$

Inserting in (7) and (8) the values of  $\alpha$  and  $\beta$  for potassium chloride we find,

$$\log \frac{s}{s_0} = 0.41 c^{0.535}; \quad (8a)$$

and for potassium iodate,

$$\log \frac{s}{s_0} = 0.456 c^{0.442}; \quad (8b)$$

and for magnesium sulfate,

$$\log \frac{s}{s_0} = 1.76 c^{0.293}. \quad (8c)$$

Using the formula given by Noyes and Falk for the freezing-point lowering we have found as shown in the foregoing paper

$$\log \frac{s}{s_0} = a c^b \quad (9)$$

where  $a$  and  $b$  are constants, an expression of the same form as that reached by means of the equation of Lewis. There is however a considerable difference between the constants in the two formulas. While in the case of uni-univalent salts  $L$  and  $\alpha$  both have values in the neighborhood of 0.4–0.5,  $a$  and  $b$  are both equal to  $1/3$ . For magnesium sulfate the difference lies in the same direction. It is remarkable however that the solubility curve of xantho chromate in magnesium sulfate calculated in

the foregoing paper according to Formula 9, gives a rather close agreement with (8c) since we have here,

$$\begin{array}{ll} L = 1.76 & a = 1.80 \\ \alpha = 0.293 & b = 0.333. \end{array}$$

### III. Uni-univalent Salts in Solvents of Other Types.

A small number of experiments has been made to find the influence of the type of the solvent upon the solubility of uni-univalent salts. The results of these experiments are given in the following tables.

TABLE XX.—PRASEO  
THIOCYANATE IN MAG-  
NESIUM SULFATE AT  $t=0$ .

$c$ .	$s \times 10^4$ .	$s/s_0$ .
0	289	
0.02	340	1.11
0.05	358	1.19
0.1	379	1.27
0.2	400	1.38

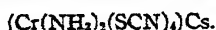
TABLE XXI.—OXALO-  
TETRAMMINE COBALTIC  
PERCHLORATE IN MAG-  
NESIUM SULFATE,  $t=0$ .

$c$ .	$s \times 10^4$ .	$s/s_0$ .
0	510	
0.05	739	1.45
0.1	823	1.61

TABLE XXII.—CROCEO  
NITRATE IN SODIUM OXA-  
LATE,  $t=0$ .

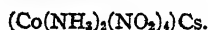
$c$ .	$s \times 10^4$ .	$s/s_0$ .
0	494	
0.02	572	1.154
0.05	621	1.256
0.1	678	1.370

TABLE XXIII.—CESIUM TETRATHIO-  
CYANATO-DIAMMINE CHROMIATE.



Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
NaOOCH	1	83.1	1.05
NaNO <sub>3</sub>	1	136.5	1.73
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.5	135.6	1.72
MgSO <sub>4</sub>	0.5	97.6	1.22
H <sub>2</sub> O		78.9	

TABLE XXIV.—CESIUM TETRANITRO-DI-  
AMMINE COBALTIATE.



Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
NaOOCH	1	785	1.47
NaNO <sub>3</sub>	1	1268	2.38
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.5	1113	2.09
MgSO <sub>4</sub>	0.5	815	1.54
H <sub>2</sub> O		532	

Comparing the data from these tables with those found for the same salts in uni-univalent solvents, we find that as a rule the solubility is mainly governed by the equivalent concentrations of the solvent, independent of its type. A solution of magnesium sulfate or of sodium oxalate dissolves just as much as a solution of a uni-univalent salt of the same equivalent concentration. The agreement between the figures is at any rate probably sufficient for establishing this rule as general, the deviations being of the same order of magnitude as found when uni-univalent solvents are mutually compared.

The values from Tables XXIII and XXIV show great diversity owing to the high concentration of the solvent employed, whereby the secondary effects are greatly increased. However, no systematic distinction between solvents of different types can be observed in these cases, either.

Because of the character of the systems no  $a$  values can be calculated here.



## IV. Bi-bivalent Salts in Bi-bivalent Solvents.

Six systems of this type have been examined. The results are given in the tables below.

TABLE XXV.—ISOTHIOCYANATO-PENTAMMINE COBALTIC CHROMATE.

(Co(NH<sub>3</sub>)<sub>5</sub>NCS)CrO<sub>4</sub>.  $s_0 = 0.001074$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>3</sup> .	<i>s/s</i> <sub>0</sub> .	<i>a</i> .
MgSO <sub>4</sub>	0.02	224	2.086	1.79
	0.05	329	3.07	1.78
	0.1	455	4.23	1.70
	0.2	673	6.26	(1.63)
	0.5	1150	10.72	(1.48)
	1.0	1770	16.48	(1.35)
				<u>1.76</u>

TABLE XXVI.—CHLORO-PENTAMMINE COBALTIC HEXACHLOROPLATINATE.

(Co(NH<sub>3</sub>)<sub>5</sub>Cl)PtCl<sub>6</sub>.  $s_0 = 0.000091$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>3</sup> .	<i>s/s</i> <sub>0</sub> .	<i>a</i> .
MgSO <sub>4</sub>	0.05	28.2	3.10	1.51
	0.1	48.3	5.31	1.73
				<u>1.62</u>

TABLE XXVII.—XANTHO CHROMATE.

(Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>)CrO<sub>4</sub>.  $s_0 = 0.000258$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>3</sup> .	<i>s/s</i> <sub>0</sub> .	<i>a</i> .
MgSO <sub>4</sub>	0.02	62	2.40	1.81
	0.05	90.8	3.52	1.79
	0.1	123.7	4.80	1.69
	0.2	180.4	6.99	(1.61)
	1.0	512.0	19.84	(1.38)
				<u>1.76</u>

TABLE XXVIII.—XANTHO OXALATE.

(Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>)C<sub>2</sub>O<sub>4</sub>.  $s_0 = 0.0001614$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>3</sup> .	<i>s/s</i> <sub>0</sub> .	<i>a</i> .
MgSO <sub>4</sub>	0.02	131	8.11	4.08
	0.05	183	11.3	3.31
	0.1	310	19.1	3.09
	0.2	445	27.6	(2.69)
	1.0	1026	63.6	(1.90)
				<u>3.5</u>

TABLE XXIX.—CHLORO-PENTAMMINE COBALTIC OXALATE. (Co(NH<sub>3</sub>)<sub>5</sub>Cl)C<sub>2</sub>O<sub>4</sub>.

$s_0 = 0.000359$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>3</sup> .	<i>s/s</i> <sub>0</sub> .	<i>a</i> .
MgSO <sub>4</sub>	0.02	238	6.63	3.90
	0.05	354	9.87	3.25
	0.1	608	16.9	3.05
	0.2	1150	32.0	(2.87)
	0.5	2040	56.8	(2.39)
	1.0	2930	81.6	(2.04)
				<u>3.4</u>

TABLE XXX.—CHLORO-PENTAMMINE CHROMIC OXALATE. (Cr(NH<sub>3</sub>)<sub>5</sub>Cl)C<sub>2</sub>O<sub>4</sub>.

$s_0 = 0.001250$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>3</sup> .	<i>s/s</i> <sub>0</sub> .	<i>a</i> .
MgSO <sub>4</sub>	0.02	596	4.77	3.60
	0.05	1014	8.11	3.20
	0.1	1706	13.65	2.98
	0.2	2640	21.10	(2.64)
	0.5	4580	36.6	(2.20)
	1.0	7070	56.6	(1.92)
				<u>3.3</u>

The *a* values are calculated according to the same equation as used in uni-univalent salts,

$$\log \frac{s}{s_0} = a (\sqrt[3]{c} - \sqrt[3]{s_0}).$$

For all the *c* and *s* calculations molal concentrations are used. The average *a* values of the first three systems, 1.71, is somewhat more than four times the *a* values for uni-univalent systems, corresponding to curves that rise much more precipitously than in the case of uni-univalent systems.

Using equivalent concentrations instead of molal concentrations in the equation we find  $a = 1.38 = 4 \times 0.34$ , instead of  $a = 1.71$ .

The three oxalates afford a very much higher increase in solubility than the other bi-bivalent salts, and correspondingly higher  $a$  values, about 3.4.

### V. Bi-bivalent Salts in Solvents of Other Types.

Bi-bivalent salts have also been determined by employing uni-uni- and uni-bivalent solvents. The results are given in Tables XXXI-XXXVI.

TABLE XXXI.—CHLORO-PENTAMMINE COBALTIC HEXACHLOROPLATINATE.

( $\text{Co}(\text{NH}_3)_5\text{Cl}$ ) $\text{PtCl}_6$ .  $s_0 = 0.000092$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KCl	0.02	13.7	1.49
	0.1	26.8	2.91
	0.15	32.7	3.55

TABLE XXXII.—CHLORO-PENTAMMINE COBALTIC OXALATE. ( $\text{Co}(\text{NH}_3)_5\text{Cl}$ ) $\text{C}_2\text{O}_4$ .

$s_0 = 0.000359$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KCl	0.02	35.9	1.47
	0.05	52.8	1.99
	0.1	71.5	2.61
	0.15	93.5	3.04
KOOCH	0.1	84.9	2.37
	0.2	111.3	3.10
	0.5	171.5	4.78
	1.0	242.4	6.76

TABLE XXXIII.—XANTHO OXALATE.

( $\text{Co}(\text{NH}_3)_5\text{NO}_2$ ) $\text{C}_2\text{O}_4$ .  $s_0 = 0.0001614$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KOOCH	0.02	27.2	1.68
	0.05	35.6	2.20
	0.1	45.5	2.82
	0.2	61.2	3.79
	0.5	96.7	5.99
	1.0	127.7	7.91
KCl	0.02	28.0	1.73
	0.05	38.2	2.36
	0.1	48.7	3.01
	0.2	70.5	4.37
	0.5	121.2	7.50
	1.0	201.1	12.4

TABLE XXXIV.—CHLORO-PENTAMMINE CHROMIC OXALATE. ( $\text{Cr}(\text{NH}_3)_5\text{Cl}$ ) $\text{C}_2\text{O}_4$ .

$s_0 = 0.00111$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KOOCH	0.02	150	1.34
	0.05	194	1.75
	0.1	254	2.29
	0.2	331	2.98
	0.5	475	4.27
	1.0	555	5.00

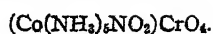
TABLE XXXV.—ISOTHIOCYANATO-PENTAMMINE COBALTIC CHROMATE.

( $\text{Co}(\text{NH}_3)_5\text{SCN}$ ) $\text{CrO}_4$ .  $s_0 = 0.00107$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KOOCH	0.02	140.2	1.31
	0.05	162.8	1.52
	0.1	189.9	1.77
NaOOCH	0.02	137.7	1.29
	0.05	157.0	1.47
	0.1	183.5	1.71

A glance at these tables and the tables in the foregoing section shows first, much more precipitous curves than found with uni-univalent solvents; second, that the rule of the equal action of equivalent normal solutions, found to hold for uni-univalent solutes, does not hold when the solute contains bivalent ions. It is evident, as appears in Fig. 2 representing the curves of solubility of xantho chromate, that a solution of a bi-bivalent

TABLE XXXVI.—XANTHO CHROMATE.



$s_0 = 0.000258$

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KOOCH	0.02	36.1	1.40	KCl	0.02	37.1	1.44
	0.05	48.0	1.86		0.05	52.0	2.02
	0.1	63.6	2.47		0.1	69.0	2.68
	0.2	81.6	3.17		0.2	88.7	3.45
	0.5	121.2	4.70	KClO <sub>3</sub>	0.02	33.2	1.28
	1.0	178.7	6.93		0.05	42.1	1.63
NaOOCH	0.02	32.3	1.25		0.1	57.0	2.21
	0.05	41.0	1.59	NaClO <sub>3</sub>	0.02	31.8	1.23
	0.1	55.8	2.16		0.05	41.7	1.61
	0.2	74.6	2.89		0.1	56.1	2.17
	0.5	113.1	4.38	KNO <sub>3</sub>	0.02	34.5	1.34
	1.0	172.9	6.70		0.05	44.4	1.72
NaCl	0.05	41.5	1.61		0.1	58.8	2.28
	0.1	56.5	2.19	NaNO <sub>3</sub>	0.02	34.4	1.33
	0.2	78.5	3.04		0.05	44.2	1.71
					0.1	57.7	2.24

salt, such as magnesium sulfate, dissolves considerably more of the bivalent solute than does an equally strong solution of a uni-univalent salt, such as potassium formate or sodium chloride. From this we can

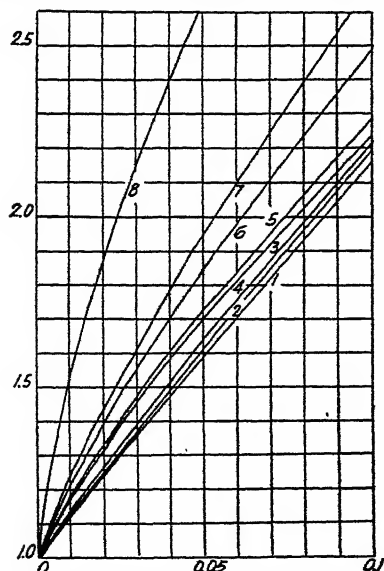


Fig. 2.—Solubility ratio  $s/s_0$  for xantho chromate in (1) NaOOCH and NaClO<sub>3</sub>, (2) NaCl, (3) KClO<sub>3</sub>, (4) NaNO<sub>3</sub>, (5) KNO<sub>3</sub>, (6) KOOCH, (7) KCl, (8) MgSO<sub>4</sub>. The abscissa indicates here and in all other diagrams equivalent concentration of the solvent.

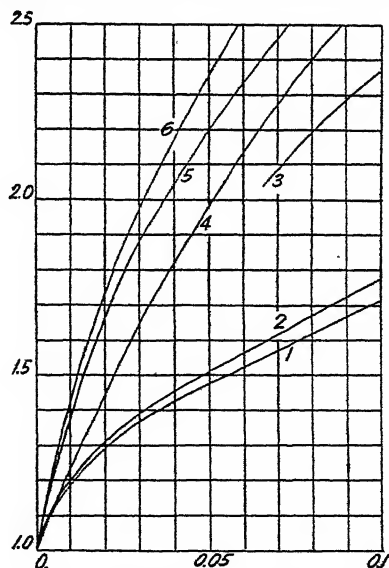


Fig. 3.—Solubility ratio  $s/s_0$  (1) Iso-thiocyanate chromate in NaOOCH, (2) Iso-thiocyanate chromate in KOOCH, (3) Pentammine oxalate in KOOCH, (4) Pentammine oxalate in KCl, (5) xantho oxalate in KOOCH, (6) xantho oxalate in KCl.

draw the conclusion that in an equal equivalent concentration of the solvent the activity coefficient of a univalent ion present in the solution is influenced to a smaller extent than is the activity coefficient of a bivalent ion. The significance of this conclusion will be clearer when considering solutes composed of ions of different valences. This is treated in the following section.

## VI. Uni-bivalent Salts in Solvents of Various Types.

The first measurements were carried out with uni-univalent solvents alone. The data are as follows.

TABLE XXXVII.—BROMO-PENTAMMINE COBALTIC BROMIDE.  $(\text{Co}(\text{NH}_3)_5\text{Br})\text{Br}_2$ .  
 $s_0 = 0.00275$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .	Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
NaOOCH	0.02	315	1.14	KOCCCCl <sub>2</sub>	0.1	388	1.41
	0.05	351	1.28		0.2	444	1.62
	0.1	393	1.43	CCl <sub>3</sub> COOH	0.1	372	1.35
	0.2	442	1.61		0.2	411	1.49
	0.5	527	1.91	KClO <sub>3</sub>	0.02	323	1.17
	1.0	593	2.16		0.05	371	1.34
KOOCH	0.02	323	1.16		0.1	425	1.54
	0.05	357	1.30	NaClO <sub>3</sub>	0.02	323	1.17
	0.1	397	1.46		0.05	369	1.34
	0.2	455	1.65		0.1	420	1.53
	0.5	549	1.98				
	1.0	648	2.36				

TABLE XXXVIII.—BROMO-PENTAMMINE COBALTIC CHLORIDE.  $(\text{Co}(\text{NH}_3)_5\text{Br})\text{Cl}_2$ .

$s_0 = 0.00542$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KClO <sub>3</sub>	0.05	699	1.29
	0.1	792	1.47
NaClO <sub>3</sub>	0.05	694	1.28
	0.1	791	1.47
	1.0	1511	2.79

TABLE XL.—CHLORO-PENTAMMINE COBALTIC CHLORIDE.  $(\text{Co}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$ .

$s_0 = 0.0091$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KOH	0.02	1090	1.20
	0.05	1320	1.45
	0.1	1310	1.44

TABLE XXXIX.—THIOCYANATO-PENTAMMINE COBALTIC IODATE.  $(\text{Co}(\text{NH}_3)_5\text{CNS})(\text{IO}_3)_2$ .  
 $s_0 = 0.00204$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
NaOOCH	0.02	230	1.13
	0.05	268	1.31
	0.1	312	1.53
	0.2	367	1.80
	0.5	488	2.39
	1.0	635	3.11
KOH	0.02	286	1.40
	0.05	324	1.59
	0.1	323	1.58

TABLE XLI.—XANTHO NITRATE.  $(\text{Co}(\text{NH}_3)_5\text{NO}_2)(\text{NO}_3)_2$ .  
 $s_0 = 0.0170$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
KCl	0.01	1784	1.05
	0.02	1858	1.09
KOOCCHCl <sub>2</sub>	0.02	1840	1.09
	0.05	2010	1.18
	0.1	2150	1.26
MgCl <sub>2</sub>	0.01	1850	1.09
Na <sub>2</sub> SO <sub>4</sub>	0.01	1970	1.16
	0.02	2210	1.30
	0.05	2720	1.60
	0.1	3360	1.97

The data represented in Figs. 4 and 5 show a somewhat stronger increase with increasing concentration of the solvent than in the case of uni-univalent salts. Otherwise the curve is almost the same, particularly as to the order of the various solvents with regard to dissolving power.

Three other salt determinations were carried out using solvents of higher types. The results from these are given in Tables XLI-XLIII and in Figs. 6, 7 and 8.

In describing the phenomena appearing in these systems it is necessary to make a sharp distinction between two cases of interaction of uni-bivalent salts. In the first of these the two salts are electrically isotypic, as for example chloropentammine bromide and calcium formate  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2$  and  $\text{Ca}(\text{OOCH})_2$ ; and in the other they are electrically heterotypic, as for example croceo sulfate and magnesium chloride,  $[\text{Co}(\text{NH}_3)_4(\text{N}-\text{O}_2)_2]_2\text{SO}_4$  and  $\text{MgCl}_2$ .

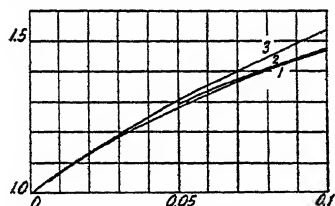


Fig. 5.—Solubility ratio of bromopentammine chloride in (1)  $\text{NaClO}_3$ , (2)  $\text{KClO}_3$ , and of thiocyanate pentammine iodate in (3)  $\text{NaOOCH}$ .

When a uni-bivalent isotypic solvent is employed, the solubility of the salt does not increase any more than when a uni-univalent one is employed. Potassium dichloro-acetate and calcium formate dissolve chloropentammine cobaltic bromide to nearly the same extent. Sodium oxalate and potassium chloride dissolve equal amounts of croceo sulfate. On the other hand using an electrically heterotypic solvent we find much greater solubilities, nearly the same as when bi-bivalent solvents are employed.

From these results and those previously given we are justified in concluding that the activity of an ion is affected similarly by ions of the same sign, only when the equivalent concentration of the acting ions is the same. If the dissolved ion is uni-univalent the action of ions of the opposite sign will likewise depend chiefly upon the equivalent concentration. In the case of dissolved ions of higher valence than unity, the effect of the ion of opposite sign will increase with increasing valence. In all cases the activity of an ion depends much more upon the nature

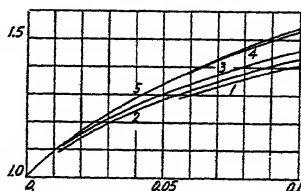


Fig. 4.—Solubility ratio of bromopentammine bromide in (1)  $\text{KOOCCl}_4$ , (2)  $\text{NaOOCH}$ , (3)  $\text{KOOCH}$ , (4)  $\text{NaClO}_3$ , (5)  $\text{KClO}_3$ .

of the solvent. When a uni-bivalent heterotypic solvent is employed, the solubility of the salt does not increase any more than when a uni-univalent one is employed. Potassium dichloro-acetate and calcium formate dissolve chloropentammine cobaltic bromide to nearly the same extent. Sodium oxalate and potassium chloride dissolve equal amounts of croceo sulfate. On the other hand using an electrically heterotypic solvent we find much greater solubilities, nearly the same as when bi-bivalent solvents are employed.

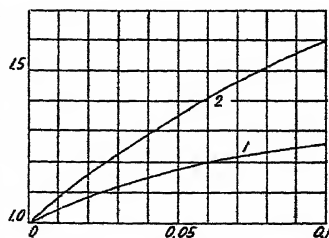


Fig. 6.—Solubility of xantho nitrate in (1)  $\text{KOOCHCl}_3$ , (2)  $\text{Na}_2\text{SO}_4$ .

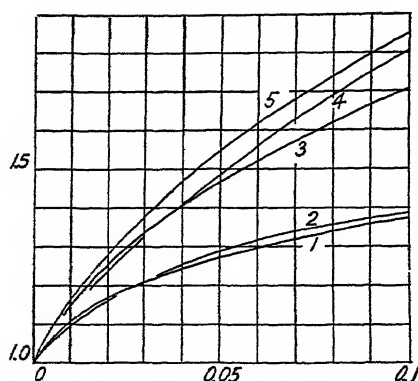


Fig. 7.—Solubility ratio of chloro-pentamine bromide in (1)  $\text{Ca}(\text{OOCH})_2$ , (2)  $\text{KOOCCCHCl}_2$ , (3)  $\text{MgSO}_4$ , (4)  $\text{Na}_2\text{SO}_4$ , (5)  $(\text{KOOCC})_2\text{C}_6\text{H}_4$ .

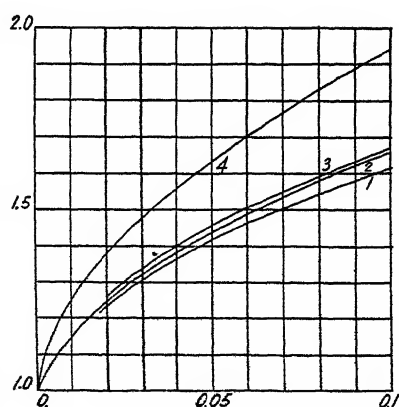


Fig. 8.—Solubility ratio of croceo sulfate in (1)  $\text{KOOCCCHCl}_2$ , (2)  $\text{KCl}$ , (3)  $\text{Na}_2\text{C}_2\text{O}_4$ , (4)  $\text{MgCl}_2$ .

of the ions of the opposite sign than on that of the ions of the same sign, a point of view of importance in the general conception of salt solutions.

TABLE XLII.—CHLORO-PENTAMINE COBALTYC BROMIDE.  $(\text{Co}(\text{NH}_2)_5\text{Cl})\text{Br}_2$ .

$s_0 = 0.00725$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
$\text{KOOCCCHCl}_2$	0.01	774	1.07
	0.05	938	1.29
	0.075	980	1.35
	0.1	1016	1.39
$\text{Ca}(\text{OOCH})_2$	0.01	815	1.12
	0.02	900	1.24
	0.04	979	1.35
	0.05	997	1.38
$(\text{KOOCC})_2\text{C}_6\text{H}_4$	0.01	932	1.29
	0.02	1073	1.48
	0.05	1340	1.85
	0.1	1604	2.21
$\text{Na}_2\text{SO}_4$	0.01	903	1.24
	0.02	1040	1.42
	0.05	1312	1.81
$\text{MgSO}_4$	0.01	916	1.26
	0.02	1027	1.40
	0.05	1245	1.72

TABLE XLIII.—CROCEO SULFATE.

$(\text{Co}(\text{NH}_2)_4(\text{NO}_2)_2)_2\text{SO}_4$ .  $s_0 = 0.00096$ .

Solvent.	$c$ .	$s \times 10^4$ .	$s/s_0$ .
$\text{KCl}$	0.01	111.5	1.16
	0.02	119.9	1.25
	0.05	138.5	1.44
	0.1	161.2	1.67
$\text{KOOCCCHCl}_2$	0.02	118.9	1.24
	0.05	136.6	1.42
	0.1	155.8	1.62
$\text{MgCl}_2$	0.01	132.6	1.38
	0.02	150.0	1.56
	0.05	185.5	1.95
	0.1	223.5	2.32
$\text{Na}_2\text{C}_2\text{O}_4$	0.01	122.2	1.26
	0.025	140.7	1.46
	0.05	161.0	1.67
	0.1	189.1	1.97

## VII. Uni-trivalent Salts in Solvents of Various Types.

The following results were obtained.

TABLE XLIV.—LUTEO TETRANITRO-DIAMMINE COBALTIATE.  $(\text{Co}(\text{NH}_3)_6)-(\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4)_2$ .  $s_0 = 0.000043$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>5</sup> .	<i>s/s</i> <sub>0</sub> .
KCl	0.01	5.23	1.22
	0.05	7.56	1.76
	0.1	9.60	2.23
MgCl <sub>2</sub>	0.01	6.36	1.48
	0.05	9.41	2.18
	0.1	11.40	2.65
Ca(OOCH) <sub>2</sub>	0.01	6.05	1.41
	0.05	8.93	2.08
	0.1	10.20	2.37
Na <sub>2</sub> SO <sub>4</sub>	0.01	10.1	2.35
	0.05	15.6	3.63
(KOOCC) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.01	11.0	2.56
	0.05	18.2	4.23
MgSO <sub>4</sub>	0.01	9.48	2.20
	0.05	14.4	3.35
	0.1	17.3	4.02

TABLE XLVI.—OXALO-TETRAMMINE CO-BALTIC HEXATHIOCYANATO CHROMIATE.  $(\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4)_2(\text{Cr}(\text{CNS})_6)$ .  $s_0 = 0.000532$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>5</sup> .	<i>s/s</i> <sub>0</sub> .
NaCl	0.001	54.9	1.03
	0.005	58.6	1.10
	0.01	62.7	1.18
	0.05	79.7	1.50
	0.1	95.4	1.79
MgCl <sub>2</sub>	0.001	57.7	1.09
	0.005	66.6	1.25
	0.01	72.8	1.37
	0.05	95.4	1.79
	0.1	110.0	2.07
Ca(OOCH) <sub>2</sub>	0.001	57.5	1.08
	0.005	66.5	1.25
	0.01	72.9	1.37
	0.05	95.4	1.79
	0.1	110.0	2.07
Na <sub>2</sub> SO <sub>4</sub>	0.001	57.5	1.08
	0.005	67.8	1.27
	0.01	77.0	1.45
	0.05	117.7	2.21
	0.1	144.0	2.71
MgSO <sub>4</sub>	0.001	58.6	1.10
	0.005	68.7	1.29
	0.01	76.6	1.44
	0.05	110.0	2.07
	0.1	144.0	2.71

TABLE XLV.—AQUO-PENTAMMINE CO-BALTIC TETRATHIOCYANATO-DIAMMINE CHROMIATE.  $(\text{Co}(\text{NH}_3)_5\text{H}_2\text{O})(\text{Cr}(\text{NH}_3)_2(\text{CNS})_4)_2$ .  $s_0 = 0.0000663$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>5</sup> .	<i>s/s</i> <sub>0</sub> .
KCl	0.01	7.32	1.10
	0.05	9.05	1.36
	0.1	10.24	1.54
MgCl <sub>2</sub>	0.005	7.41	1.11
	0.01	8.12	1.22
	0.1	11.84	1.77
Ca(OOCH) <sub>2</sub>	0.005	8.61	1.29
	0.01	9.76	1.46
	0.05	12.0	1.80
Na <sub>2</sub> SO <sub>4</sub>	0.1	13.6	2.04
	0.005	11.0	1.65
	0.01	12.6	1.86
(KOOCC) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.05	19.8	2.98
	0.005	12.3	1.85
	0.01	14.1	2.12
MgSO <sub>4</sub>	0.1	27.2	4.08
	0.01	11.5	1.72
	0.1	18.6	2.79

TABLE XLVII.—PRASEO HEXACYANO FERRIATE.  $(\text{Co}(\text{NH}_3)_4\text{Cl}_2)_2(\text{Fe}(\text{CN})_6)_3$ .  $s_0 = 0.000121$ .

Solvent.	<i>c</i> .	<i>s</i> × 10 <sup>5</sup> .	<i>s/s</i> <sub>0</sub> .
KCl	0.01	13.9	1.15
	0.05	19.3	1.60
	0.1	23.3	1.93
MgCl <sub>2</sub>	0.005	15.7	1.30
	0.01	17.1	1.41
	0.05	23.1	1.91
Ca(OOCH) <sub>2</sub>	0.1	26.1	2.16
	0.01	16.8	1.39
	0.05	23.0	1.91
Na <sub>2</sub> SO <sub>4</sub>	0.1	26.3	2.18
	0.005	13.8	1.14
	0.01	15.8	1.30
(KOOCC) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.05	22.2	1.84
	0.1	26.5	2.19
	0.005	14.4	1.19
MgSO <sub>4</sub>	0.01	16.0	1.32
	0.05	22.7	1.88
	0.1	28.2	2.33
MgSO <sub>4</sub>	0.005	14.9	1.23
	0.01	16.7	1.38
	0.05	22.2	1.84
MgSO <sub>4</sub>	0.1	25.1	2.08

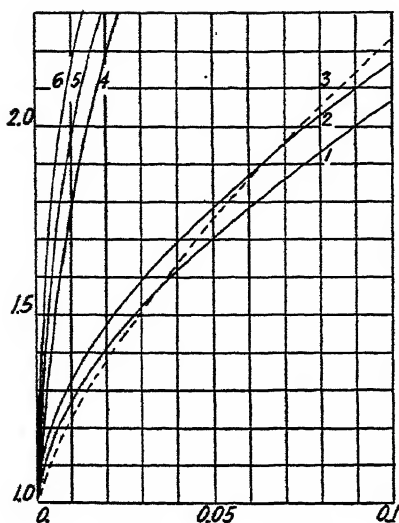


Fig. 9.—Solubility ratio of luteo tetra-nitro cobaltate in (1)  $\text{Ca}(\text{OOCH})_2$ , (2)  $\text{MgCl}_2$ , (3)  $\text{KCl}$ , (4)  $\text{MgSO}_4$ , (5)  $\text{Na}_2\text{SO}_4$ , (6)  $(\text{KOOC})_2\text{C}_6\text{H}_4$ .

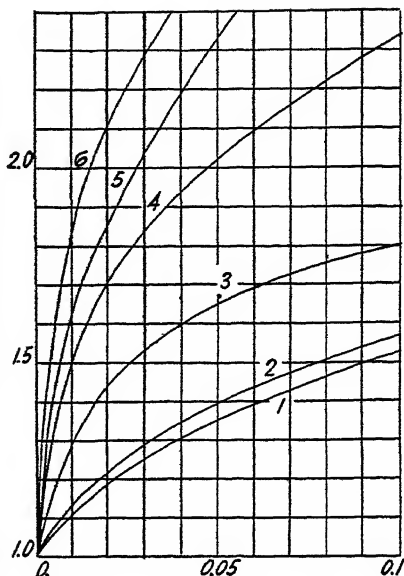


Fig. 10.—Solubility ratio of aquo-pentamine tetrathiocyanate chromiate in (1)  $\text{KCl}$ , (2)  $\text{MgCl}_2$ , (3)  $\text{Ca}(\text{OOCH})_2$ , (4)  $\text{MgSO}_4$ , (5)  $\text{Na}_2\text{SO}_4$ , (6)  $(\text{KOOC})_2\text{C}_6\text{H}_4$ .

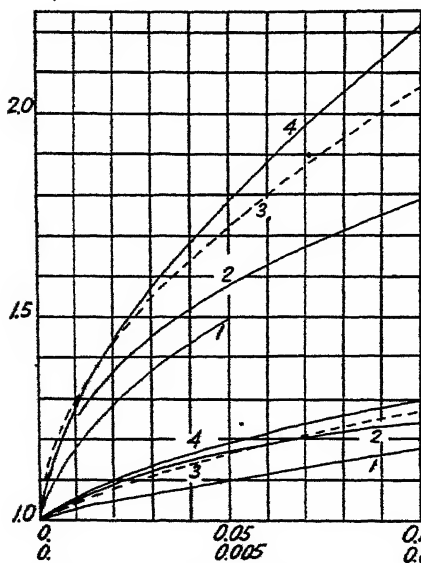


Fig. 11.—Solubility ratio of oxalo-hexa-thio-cyanato chromiate in (1)  $\text{NaCl}$ , (2)  $\text{MgCl}_2$  and  $\text{Ca}(\text{OOCH})_2$ , (3)  $\text{Na}_2\text{SO}_4$ , (4)  $\text{MgSO}_4$ .

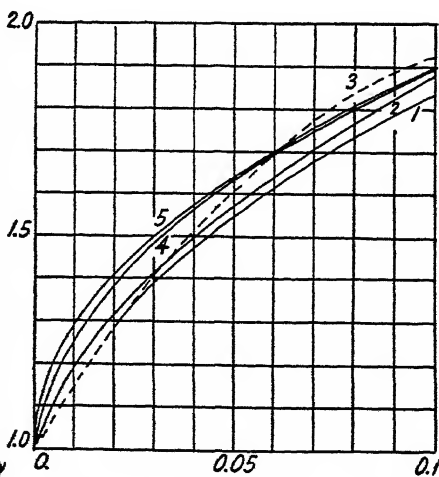


Fig. 12.—Solubility ratio of praseo hexa-cyano ferriate in (1)  $\text{Na}_2\text{SO}_4$ , (2)  $(\text{KOOC})_2\text{C}_6\text{H}_4$ , (3)  $\text{KCl}$ , (4)  $\text{Ca}(\text{OOCH})_2$ , (5)  $\text{MgCl}_2$ .



The curves are shown in Figs. 9, 10, 11 and 12. In the case of luteo-tetranitro-diammine cobaltiate we encounter the same effect of the electric type of solute and solvent as in the case of uni-bivalent salts, but to a still more marked degree. When the solvent contains bivalent anions the solubility is increased very much more than when it contains bivalent cations, in accordance with the principle developed in the foregoing section.

Roseo-tetrathiocyanato chromiate exhibits the same behavior towards solvents of different electrical type. Here, however, the individual influence of the solvents proves to be more marked. Only the curves for magnesium chloride and potassium chloride are nearly coincident.

The diagrams for the two salts with trivalent anions show this less conspicuously. The greater dissolving power of the bivalent cation as compared to the bivalent anion is still noticeable but only in the most diluted solutions. With rising concentration the individual nature of the solvent seems to play a considerable part in the action, obscuring to a certain degree the pure primary electrical effect. The diagram of praseo-hexacyano ferriate is particularly difficult to account for from the point of view adopted here. On account of the instability of the saturating salt the data are probably not very reliable.

### VIII. Tri-trivalent Salts in Solvents of Various Types.

TABLE XLVIII.—LUTEO HEXACYANO COBALTIATE.  $(\text{Co}(\text{NH}_3)_6)(\text{Co}(\text{CN})_6)$ .

Solvent.	$s_0 = 0.0000070$ .		
	$c$ .	$s \times 10^3$ .	$s/s_0$ .
KCl	0.05	3.79	5.4
	0.1	6.50	9.3
	0.2	12.46	17.8
	0.5	34.7	49.6
	0.75	56.2	80.3
	1.0	81.3	116
	2.0	207	296
NaCl	0.1	6.02	8.6
	1.0	60.2	86
NaOOCH	0.2	12.16	12.4
	0.5	26.32	26.8
	1.0	48.82	49.8
KOOCH	0.2	13.77	14.0
	0.5	34.02	34.7
	1.0	71.35	72.8
$\text{MgSO}_4$	0.05	24.3	22.7
	0.1	39.0	39.8
	1.0	277	282

TABLE XLIX.—LUTEO HEXACYANO FERRIATE.  $(\text{Co}(\text{NH}_3)_6)(\text{Fe}(\text{CN})_6)$ .

Solvent.	$s_0 = 0.0000098$ .		
	$c$ .	$s \times 10^3$ .	$s/s_0$ .
KCl	0.05	5.34	5.4
	0.1	9.11	9.3
	0.2	17.24	17.3
	0.5	46.2	47.2
	0.75	75.1	76.5
	1.0	107.9	110
	2.0	272	277
NaCl	0.1	8.31	8.5
	1.0	79.1	81

TABLE L.—LUTEO TRIOXALO COBALTIATE.  $(\text{Co}(\text{NH}_3)_6)(\text{Co}(\text{C}_2\text{O}_4)_3)$ .

Solvent.	$s_0 = 0.000019$		
	$c$ .	$s \times 10^3$ .	$s/s_0$ .
NaCl	0.05	10.14	5.3
	0.1	17.8	9.4
	0.2	34.8	18.3
	0.5	100.8	53.1
	1.0	245	129

In this series the increase in solubility is very much higher than in the foregoing, as shown in Table XLVIII-L, and the accompanying diagram.

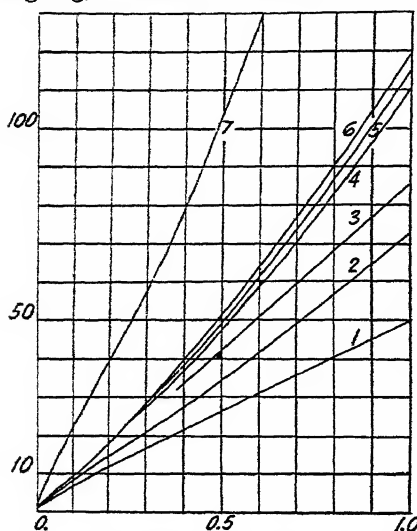


Fig. 13.—Solubility ratio of luteo hexacyano cobaltate in (1)  $\text{NaOOCH}$ , (2)  $\text{KOOCH}$ , (3)  $\text{NaCl}$ , (5)  $\text{KCl}$ , (7)  $\text{MgSO}_4$ , and of luteo hexacyano ferriate in (4)  $\text{KCl}$ , and of luteo trioxalo cobaltate in (6)  $\text{NaCl}$ .

salt, indicating that the solubility increases more than in proportion to the increase in the concentration of potassium chloride.

Magnesium sulfate again gives sharply rising solubility curves for tri-

<sup>6</sup> An attempt was made to determine the solubility of luteo-trioxalo cobaltate in  $\text{KCl}$  solution as well. While with  $\text{NaCl}$  as solvent, green solutions are obtained, the color of which is due to the  $\text{CoOx}_3^{---}$  ion,  $\text{KCl}$  gives yellow solutions evidently not containing the complex ion. The phenomenon is explained by assuming the existence of the double salt:  $\text{K}_2[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]_2 \cdot 6\text{H}_2\text{O}$  described by S. P. L. Sørensen ("Studier over Koboltidoxalater," Copenhagen, 1899, p. 71). As no corresponding sodium double salt is formed under the same condition and the potassium salt is very sparingly soluble, this peculiar reaction probably could be used for the separation of the two alkali metals.

<sup>7</sup> The agreement in properties of salts of the ions  $\text{Co}(\text{CN})_6^{---}$  and  $\text{Fe}(\text{CN})_6^{---}$  are well-known. It is probable, however, that a careful scrutiny will show much more concordance than hitherto assumed. According to Werner's theory, we have in both cases in octahedral arrangement of  $\text{CN}$  groups around a central  $\text{Co}$  or  $\text{Fe}$  atom. Just as with the nucleus in isotopic atoms, the central atom in these groups is shielded from reaction with outside atoms or groups if the distances between the central atom and the coordinated groups are the same. The figures for the specific weight of  $\text{K}_2\text{Fe}(\text{CN})_6$  and  $\text{K}_2\text{Co}(\text{ON})_6$  prove that this holds very approximately, the distances in the  $\text{Fe}$  compound exceeding those in the  $\text{Co}$  compound by less than 2%.

The curves for luteo-hexacyano cobaltate and ferriate exhibit a remarkable concordance, and the absolute solubilities are also very nearly the same.<sup>7</sup>

Also the shape of the solubility curve of the trioxalo cobaltate shows a close agreement with that of the cyanides. The first mentioned curve is however steeper, showing that the activity of the trioxalo cobaltate ion is lessened by the solvent more than is the activity of the two others.

A saturated solution of luteo hexacyano cobaltate in 3 *N* potassium chloride solution gives on dilution with water to 0.5 *N* in a short time a precipitate of the solid luteo

trivalent salts. In 0.1 *M* solution the solubility of luteo-hexacyano cobaltate is 40 times as great as in pure water.

In accordance with the theoretical shape of the solubility curves for tri-trivalent salts shown in the first paper of this series, all the curves for these salts are more like straight lines than those found with salts of lower types. That the individual nature of the solvent is here found to be much more pronounced than in the case of uni-univalent salts is likewise in agreement with the theory requiring changes in  $s/s_0$ , which for the same percentage change in the coefficient  $a$ , are greater in proportion to the absolute value of  $a$ .

### IX. General Remarks.

In the first paper of this series the expression

$$\log \frac{s}{s_0} = a (\sqrt[3]{c_1} - \sqrt[3]{s_0})$$

was chosen to cover approximately the solubility changes of salts in hetero-ionic solvents up to about 0.1 *N* solution,  $a$  being here a constant, which in uni-univalent salt systems has a value of about  $1/3$ . The experimental material in salt systems of the same type used in the present paper agrees approximately with the established equation, and an equation of the same structure seems to hold in the case of bivalent salt systems as well. However the individual behavior of the salt employed is more pronounced in the more developed material now at hand, and tends to obscure any numerical regularity in salt systems of promiscuous type. On the basis of the above experiments the following qualitative rules may be formulated. *The influence of the solvent increases with the increasing valence of the ion of the solvent salt, which in the case of the tri-bivalent salts leads to an enormous increase of solubility, even on the addition of solvents of very low concentration. When both the dissolved and dissolving ions are of the higher valence, the effect of the sign of the electric charge is very marked, producing the highest solubility values when the polyvalent ions of solvent and solute are of different sign.*

As already indicated in the first paper, the reason for the appearance of individuality in the solubility curves must be sought partly in the hydration of the solvent and the solute, and partly in the fact that in these ions we are dealing not with mass as points, but with particles of different sizes bearing a number of electric charges of opposite signs, the algebraic sum of which gives the net charge or valence of the ion.

It is probable that this influence of size of ion, especially in the field of metal ammonia salts considered in this paper, on account of the rather complicated molecular structure of these salts will in many cases prove to be of considerable magnitude.

Since the theory of solubility as here developed, showing the dependence of solubility on the solvent, is really nothing but a theory of solutions, the proper way of attacking the problem, when its complicated nature has been thus manifested, will be a more detailed systematic examination of single cases of equilibrium, rather than the broad consideration of an elaborate mass of material, such as is given in the present paper. The knowledge now available as to the general behavior of salts as saturating substances in salt solution is, however, of great value in such a closer study of single cases. The conclusive results achievable from experiments in this direction will be the subject matter of the next article in this series.

COPENHAGEN, DENMARK.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

## THE CRYSTAL STRUCTURE OF AMMONIUM CHLOROPLATINATE.

BY RALPH W. G. WYCKOFF AND EUGEN POSNJAK.

Received June 24, 1921.

**Introduction.**—This study of the crystal structure of ammonium chloroplatinate is intended primarily to furnish an illustration of the application of that method of studying the structures of crystals which arises from the use of the theory of space groups.<sup>1</sup> At the same time it will show the possibilities and more especially the present limitations in the study of any but the very simplest of structures.

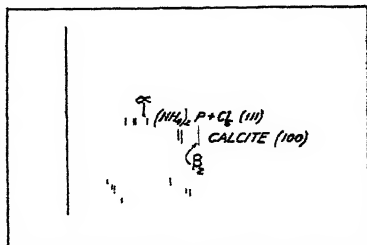
**Outline of the Determination.**—The study of the arrangement of the atoms in this crystal will be carried out through the following main steps: (1) a consideration of the X-ray reflection spectrum from some important crystal face, in order to determine the absolute dimensions of the unit cell and to indicate the number of chemical molecules to be associated with it; (2) a description, with the aid of the results of (1), the crystallographic data, and the theory of space groups, of all of the ways in which it is possible for the atoms of ammonium chloroplatinate to be arranged; (3) the obtaining of diffraction data suitable for distinguishing between these various possible structures and the determination of the correct one to represent the arrangement of the atoms within the crystals of this salt.

**The Specimens.**—The crystals that were employed for this investigation are clear octahedrons 2 to 3 mm. on their largest diameters. They were sufficiently small so that the Laue photographs, to be described later, were prepared by passing the X-rays through the entire crystal without

<sup>1</sup> P. Niggli, "Geometrische Krystallographie des Discontinuums," Leipzig, 1919; Ralph W. G. Wyckoff, *Am. J. Sci.*, 1, 127 (1921) and earlier papers.

first cutting a thin section. Owing to the fact that the crystals were smaller than the pin-hole beam of X-rays, the spots of these photographs were no longer elliptical but bore a shape that was conditioned by the shape of the crystal. The reflection spectra were obtained from faces that were not more than 2 mm. on a side. It is of interest to note that satisfactory data for the determination of the structure of a crystal at least in some instances can be obtained from such small crystals.

**The Reflection Spectrum and the Number of Chemical Molecules within the Unit Cell.**—A comparison X-ray spectrum from the cleavage (100) face of calcite and from the octahedral (111) face of ammonium chloroplatinate was prepared in the usual manner by mounting the two crystals one above the other upon the rotating table of an X-ray spectrometer. The radiation was taken from a tungsten tube. The drawing of Fig. 1 shows the spectra that were thus obtained.<sup>2</sup> Knowing



the wave lengths of the reflected X-rays and also the spacing of calcite against the (100) plane, it is possible from the measurement of its spectrum to eliminate errors in the spectrograph used by calculating in the following manner the distance from the crystal to the photographic plate.

TABLE I.  
THE CALCITE SPECTRUM FROM THE (100) FACE.  
 $d/n = 3.0281 \times 10^{-8}$  cm.<sup>4</sup>

Line.	Wave length $\times 10^{-8}$ cm.	Distance (a) (on plate). Cm.	$\sin \theta$ .	$\tan \theta$ .	Distance (b) (crystal-plate). Cm.
$\beta_2$	1.242	4.34	0.2048	0.4377	9.91 <sup>5</sup>
$\gamma_1$	1.095	3.78	0.1807	0.3804	9.93 <sup>7</sup>
$\gamma_2, \gamma_3$	1.061	3.64	0.1751	0.3674	9.90 <sup>7</sup>

9.91<sup>7</sup>

By rearrangement of the equation  $n\lambda = 2d \sin \theta$ ,<sup>3</sup> it is seen that  $\sin \theta = n\lambda/2d$ ; furthermore  $\tan 2\theta$  gives the ratio of (a) the distance of a spectrum line from the central image upon the photographic plate and (b) the dis-

<sup>2</sup> Partly because of the comparatively long time that was required to obtain a satisfactory spectrum, the resulting photograph was so blackened by scattered radiation that its reproduction would not have been satisfactory. The drawing of Fig. 1 is made from a tracing of this spectrum.

<sup>3</sup> In this equation as usual  $n$  = the order of the reflection,  $\lambda$  = the wave length of the reflected X-rays,  $d$  = the spacing between like reflecting planes, and  $\theta$  the angle of the reflection.

<sup>4</sup> W. Duane, Nat. Research Council, *Bull.*, 1, 383 (1920).

tance from the crystal to the photographic plate. This latter distance ( $b$ ) can thus be calculated for this particular spectrum from the spectrum of calcite (Table I, p. 2293).

Since  $d/n = \frac{1}{2\lambda} \sin \Theta$ , the reflection from the (111) face of ammonium chloroplatinate can be calculated in a similar manner (Table II).

TABLE II.  
THE AMMONIUM CHLOROPLATINATE SPECTRUM FROM THE (111) FACE.

Line.	Wave length $\times 10^{-8}$ cm.	Distance ( $a$ ) (on plate). Cm.	$\tan 2\Theta$ .	$\sin \Theta$ .	$(d/n)_m$ . Cm.
$\alpha_1$	1.473	2.63	0.2652	0.1293	$5.690 \times 10^{-8}$
$\beta_1$	1.278	2.28	0.2299	0.1127	5.668
$\beta_2$	1.242	2.20	0.2218	0.1089	5.696
$\gamma_1$	1.095	1.94	0.1956	0.0964	5.678

5.683  $\times 10^{-8}$

The number of chemical molecules associated with the unit cell of a cubic crystal, or rather, since the order of the observed reflection cannot be told with any degree of assurance, the ratio of the number of molecules to the cube of the order of the reflection,  $m/n^3$ , can be obtained from the following expression,

$$m/n^3 = \frac{(d/n)_{100}^3 \times \rho}{M}, \quad (1)$$

where  $M$ , the mass of a chemical molecule of the salt is equal to its molecular weight multiplied by the weight of an atom whose atomic weight is unity (roughly equal to the weight of a single atom of hydrogen =  $1.64 \times 10^{-24}$  g.), and  $\rho$  = the density of the crystal. The spacing of any plane ( $hkl$ ) is related to the spacing of the cube (100) plane of a cubic crystal by the following equation,

$$d_{hkl} = \frac{d_{100}}{\sqrt{h^2 + k^2 + l^2}}. \quad (2)$$

Substituting in Equation 1 the value of  $d_{100}$  obtained by transposing Equation 2, the value of  $m/n^3$  for a cubic crystal can be calculated from the measurement of the reflection spectrum from any crystal face through

$$m/n^3 = \frac{(d/n)_{hkl}^3 \times (h^2 + k^2 + l^2)^{3/2} \times \rho}{M}. \quad (3)$$

The values of the density of ammonium chloroplatinate which have been recorded are sufficiently discordant so that a redetermination seemed desirable. Using a pycnometer method<sup>5</sup> the density at 30° against water at 4° was found to be 3.065. The substitution of the appropriate values for ammonium chloroplatinate in Equation 3 gives for  $m/n^3$  the value of 4.021. If this value is considered in the light of a table giving values for

<sup>5</sup> J. Johnston and L. H. Adams, THIS JOURNAL, 34, 566 (1912).

$m/n^3$  for all possible values of  $m$  and  $n$ , it becomes evident that in this case either<sup>6</sup>  $m=4$  and  $n=1$ , or  $m=32$  and  $n=2$ .

If  $n=1$  then the application of Expression 2 to the spacing calculated for the (111) planes gives a length of the side of the unit cube of  $d_{110} = d_{111} \times \sqrt{3} = 9.843 \times 10^{-8}$  cm. If, however,  $n=2$ , this dimension is twice as great, namely,  $19.686 \times 10^{-8}$  cm.

**The Possible Arrangements for the Atoms in Ammonium Chloroplatinate.**—From a knowledge of all of the special cases of the space groups it is possible to write down all of the ways in which the atoms of ammonium chloroplatinate can be arranged within the unit cube, if the class of symmetry to which the crystal should be assigned is known.

Etch figures upon different faces of crystals of this salt have been studied,<sup>7</sup> so that from the standpoint of the crystallographer its *symmetry* is quite definitely established as that of the normal, or holohedral, class of the cubic system. Ammonium chloroplatinate must then be assigned to one of the 10 space groups,  $O_h^{1-10}$ , which possess this symmetry.

Two cases arise, one if it is assumed that  $m=4$  and  $n=1$ , the other if it is assumed that  $m=32$  and  $n=2$ . They will be discussed separately as follows.<sup>8</sup>

*I. Assuming that  $m=4$ ,  $n=1$ .* In Table III are stated the number and nature of the special cases of each of the 10 space groups  $O_h^{1-10}$ . The number outside of the parenthesis is the number of special cases having a particular number of equivalent positions (for like atoms) within the unit cell; the number in parenthesis is the number of variable parameters possessed by these arrangements.

Since ammonium chloroplatinate has the formula  $(NH_4)_2PtCl_6$  and since it is assumed here that 4 chemical molecules are to be contained within the unit cube, this cell must contain 4 platinum atoms, 8 nitrogen atoms, 24 chlorine atoms and 32 hydrogen atoms. An inspection of Table III shows that there are but two ways of arranging the 4 platinum atoms within the unit; (1) 3 of them must be alike and different from the fourth, both chemically and crystallographically; or (2) all 4 must be alike. If the 4 platinum atoms are not all alike (1), then the positions of the atoms within the unit cube must be those of special cases of the space group  $O_h^1$ ; otherwise (2) they must be assigned to either space group  $O_h^4$  or space group  $O_h^5$ . There is every reason to believe that the 4 platinum atoms are chemically, and hence also crystallographically, all alike (2). For the sake of completeness, however, both possibilities will be listed at this point. All of the special cases of these three space groups,  $O_h^1$ ,  $O_h^4$  and

<sup>6</sup> Ralph W. G. Wyckoff, *Am. J. Sci.*, 1, 138 (1921).

<sup>7</sup> A. Ries, *Z. Kryst. Min.*, 36, 321 (1902).

<sup>8</sup> The data for this discussion are taken from unpublished tables giving all of the special cases of the space groups.

TABLE III.  
THE SPECIAL CASES OF THE CUBIC HOLOHEDRAL SPACE GROUPS.

No. of equivalent positions.	Space group.				No. of equivalent positions.	Space group.		
	1. $O_h$ .	2. $O_h$ .	3. $O_h$ .	4. $O_h$ .		5. $O_h$ .	6. $O_h$ .	7. $O$ .
1	2(0)	....	....	....	1	....	....	....
2	....	1(0)	1(0)	1(0)	2	....	....	....
3	2(0)	....	....	....	3	....	....	....
4	....	....	....	2(0)	4	2(0)	....	....
6	2(1)	1(0)	3(0)	1(0)	6	....	....	....
8	1(1)	1(0)	1(0)	1(1)	8	1(0)	2(0)	2(0)
12	3(1)	1(0); 1(1)	3(1)	1(0); 1(1)	12	....	....	....
16	....	1(1)	1(1)	....	16	....	....	2(0)
24	3(2)	2(1)	1(1); 1(2)	2(1); 1(2)	24	1(0); 1(1)	2(0)	....
32	....	....	....	....	32	1(1)	....	1(1)
48	1(3)	1(3)	1(3)	1(3)	48	3(1)	2(1)	2(1)
64	....	....	....	....	64	....	1(1)	....
96	....	....	....	....	96	2(2)	1(1); 1(2)	1(1); 1(2)
192	....	....	....	....	192	1(3)	1(3)	1(3)

No. of equivalent positions.	Space Group.		
	8. $O_h$ .	9. $O_h$ .	10. $O_h$ .
1	....	....	....
2	....	1(0)	....
3	....	....	....
4	....	....	....
6	....	1(0)	....
8	....	1(0)	....
12	....	1(0); 1(1)	....
16	1(0)	1(1)	2(0)
24	....	2(1)	2(0)
32	2(0)	....	1(1)
48	1(0)	1(1); 2(2)	2(1)
64	1(1)	....	....
96	2(1)	1(3)	1(3)
192	1(3)	....	....

$O_h^2$  (through 32 equivalent positions, the maximum number of like atoms possible within the unit cell) are as follows.

Space Group  $O_h^1$ .

One equivalent position

1a. 000.

1b.  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

Three equivalent positions

3a.  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

3b.  $\frac{1}{2}00$ ;  $0\frac{1}{2}0$ ;  $00\frac{1}{2}$ .

Six equivalent positions

6a.  $u00$ ;  $0u0$ ;  $00u$ ;  $\bar{u}00$ ;  $0\bar{u}0$ ;  $00\bar{u}$ .

6d.  $u\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}u\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}u$ ;  $\bar{u}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\bar{u}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\bar{u}$ .



*Eight equivalent positions*8c.  $uuu; u\bar{u}\bar{u}; \bar{u}u\bar{u}; \bar{u}\bar{u}u; \bar{u}uu; u\bar{u}u; u\bar{u}\bar{u}; u\bar{u}\bar{u}$ .*Twelve equivalent positions*12f.  $u0\frac{1}{2}; \bar{u}0\frac{1}{2}; u\frac{1}{2}0; \bar{u}\frac{1}{2}0; \frac{1}{2}u0; \frac{1}{2}\bar{u}0;$  $0u\frac{1}{2}; 0\bar{u}\frac{1}{2}; 0\frac{1}{2}u; 0\frac{1}{2}\bar{u}; \frac{1}{2}0u; \frac{1}{2}0\bar{u}.$ 12m.  $u\bar{u}0; u\bar{u}0; \bar{u}u0; \bar{u}u0; 0u\bar{u}; 0u\bar{u};$  $0\bar{u}\bar{u}; 0\bar{u}\bar{u}; \bar{u}0u; \bar{u}0u; u0\bar{u}; u0\bar{u}.$ 12n.  $u\bar{u}\frac{1}{2}; u\bar{u}\frac{1}{2}; \bar{u}u\frac{1}{2}; \bar{u}u\frac{1}{2}; \frac{1}{2}u\bar{u}; \frac{1}{2}u\bar{u};$  $\frac{1}{2}\bar{u}\bar{u}; \frac{1}{2}\bar{u}\bar{u}; \bar{u}\frac{1}{2}u; \bar{u}\frac{1}{2}u; \bar{u}\frac{1}{2}\bar{u}; \bar{u}\frac{1}{2}\bar{u}.$ *Twenty-four equivalent positions*24o.  $0uv; 0\bar{u}\bar{v}; 0u\bar{v}; 0\bar{u}v; v0u; \bar{v}0\bar{u};$  $\bar{v}0u; v0\bar{u}; uv0; \bar{u}\bar{v}0; u\bar{v}0; \bar{u}v0;$  $u0\bar{v}; \bar{u}0\bar{v}; u0\bar{v}; \bar{u}0\bar{v}; 0vu; 0\bar{v}\bar{u};$  $0\bar{v}u; 0v\bar{u}; vu0; \bar{v}\bar{u}0; \bar{v}u0; v\bar{u}0.$ 24p.  $\frac{1}{2}uv; \frac{1}{2}\bar{u}\bar{v}; \frac{1}{2}u\bar{v}; \frac{1}{2}\bar{u}v; v\frac{1}{2}u; \bar{v}\frac{1}{2}\bar{u};$  $\bar{v}\frac{1}{2}u; v\frac{1}{2}\bar{u}; uv\frac{1}{2}; \bar{u}\bar{v}\frac{1}{2}; u\bar{v}\frac{1}{2}; \bar{u}v\frac{1}{2};$  $u\frac{1}{2}v; \bar{u}\frac{1}{2}\bar{v}; u\frac{1}{2}\bar{v}; \bar{u}\frac{1}{2}v; \frac{1}{2}vu; \frac{1}{2}\bar{v}\bar{u};$  $\frac{1}{2}\bar{v}u; \frac{1}{2}v\bar{u}; v\frac{1}{2}\bar{u}; \bar{v}\frac{1}{2}u; \bar{v}u\frac{1}{2}; v\bar{u}\frac{1}{2}.$ 24q.  $uu\bar{v}; u\bar{u}\bar{v}; \bar{u}u\bar{v}; \bar{u}\bar{u}v; vu\bar{u}; \bar{v}u\bar{u};$  $\bar{v}\bar{u}\bar{u}; v\bar{u}\bar{u}; uv\bar{u}; \bar{u}\bar{v}u; u\bar{v}\bar{u}; \bar{u}v\bar{u};$  $\bar{u}\bar{u}\bar{v}; \bar{u}uv; u\bar{u}\bar{v}; u\bar{u}\bar{v}; \bar{v}\bar{u}\bar{u}; \bar{v}\bar{u}\bar{u};$  $v\bar{u}\bar{u}; \bar{v}u\bar{u}; \bar{u}\bar{v}\bar{u}; uv\bar{u}; \bar{u}\bar{v}u; u\bar{v}u.$ Space Group  $O_h^4$ .*Two equivalent positions*2a.  $000; \frac{1}{2}\frac{1}{2}\frac{1}{2}.$ *Four equivalent positions*4d.  $\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}.$ 4e.  $\frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}.$ *Six equivalent positions*6e.  $0\frac{1}{2}0; 00\frac{1}{2}; \frac{1}{2}00; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}.$ *Eight equivalent positions*8d.  $uuu; \bar{u}\bar{u}\bar{u}; \frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-u; u+\frac{1}{2}, \frac{1}{2}-u, u+\frac{1}{2};$  $u\bar{u}\bar{u}; \bar{u}\bar{u}u; \frac{1}{2}-u, u+\frac{1}{2}, u+\frac{1}{2}; u+\frac{1}{2}, u+\frac{1}{2}, \frac{1}{2}-u.$ *Twelve equivalent positions*12h.  $\frac{1}{2}0\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}\frac{1}{2}0;$  $\frac{1}{2}\frac{1}{2}0; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}0\frac{1}{2}.$ 12a.  $u00; \bar{u}00; 0u0; u+\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}-u, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, u+\frac{1}{2}, \frac{1}{2};$  $0\bar{u}0; 00u; 00\bar{u}; \frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, u+\frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u.$ *Twenty-four equivalent positions*24f.  $u0\frac{1}{2}; u\frac{1}{2}0; \frac{1}{2}u0; u+\frac{1}{2}, \frac{1}{2}, 0; u+\frac{1}{2}, 0, \frac{1}{2}; 0, u+\frac{1}{2}, \frac{1}{2};$  $0u\frac{1}{2}; 0\frac{1}{2}u; \frac{1}{2}0u; \frac{1}{2}, u+\frac{1}{2}, 0; \frac{1}{2}, 0, u+\frac{1}{2}; 0, \frac{1}{2}, u+\frac{1}{2};$  $\bar{u}0\frac{1}{2}; \bar{u}\frac{1}{2}0; \frac{1}{2}\bar{u}0; \frac{1}{2}-u, \frac{1}{2}, 0; \frac{1}{2}-u, 0, \frac{1}{2}; 0, \frac{1}{2}-u, \frac{1}{2};$  $0\bar{u}\frac{1}{2}; 0\frac{1}{2}\bar{u}; \frac{1}{2}0\bar{u}; \frac{1}{2}, \frac{1}{2}-u, 0; \frac{1}{2}, 0, \frac{1}{2}-u; 0, \frac{1}{2}, \frac{1}{2}-u.$ 24t.  $u, \frac{1}{2}-u, \frac{1}{2}; u, u+\frac{1}{2}, \frac{1}{2}; \bar{u}, \frac{1}{2}-u, \frac{1}{2}; \bar{u}, u+\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, u, \frac{1}{2}-u; \frac{1}{2}, u, u+\frac{1}{2};$  $\frac{1}{2}, \bar{u}, \frac{1}{2}-u; \frac{1}{2}, \bar{u}, u+\frac{1}{2}; \frac{1}{2}-u, \frac{1}{2}, u; u+\frac{1}{2}, \frac{1}{2}, u; \frac{1}{2}-u, \frac{1}{2}, \bar{u}; u+\frac{1}{2}, \frac{1}{2}, \bar{u};$  $\frac{1}{2}-u, u, \frac{1}{2}; u+\frac{1}{2}, u, \frac{1}{2}; \frac{1}{2}-u, \bar{u}, \frac{1}{2}; u+\frac{1}{2}, \bar{u}, \frac{1}{2}; u, \frac{1}{2}, \frac{1}{2}-u; u, \frac{1}{2}, u+\frac{1}{2};$  $\bar{u}, \frac{1}{2}, \frac{1}{2}-u; \bar{u}, \frac{1}{2}, u+\frac{1}{2}; \frac{1}{2}, \frac{1}{2}-u, u; \frac{1}{2}, u+\frac{1}{2}, u; \frac{1}{2}, \frac{1}{2}-u, \bar{u}; \frac{1}{2}, u+\frac{1}{2}, \bar{u}.$ 24u.  $uu\bar{v}; u\bar{u}\bar{v}; \bar{u}u\bar{v}; \frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-v; \frac{1}{2}-u, u+\frac{1}{2}, v+\frac{1}{2}; u+\frac{1}{2}, \frac{1}{2}-u, v+\frac{1}{2};$  $\bar{u}\bar{u}\bar{v}; v\bar{u}\bar{v}; \bar{v}u\bar{v}; u+\frac{1}{2}, u+\frac{1}{2}, \frac{1}{2}-v; \frac{1}{2}-v, \frac{1}{2}-u, \frac{1}{2}-u; v+\frac{1}{2}, \frac{1}{2}-u, u+\frac{1}{2};$  $\bar{v}\bar{u}\bar{u}; v\bar{u}\bar{u}; uv\bar{u}; v+\frac{1}{2}, u+\frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}-v, u+\frac{1}{2}, u+\frac{1}{2}; \frac{1}{2}-u, \frac{1}{2}-v, \frac{1}{2}-u;$  $\bar{u}\bar{v}u; u\bar{v}\bar{u}; \bar{u}\bar{v}\bar{u}; u+\frac{1}{2}, v+\frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}-u, v+\frac{1}{2}, u+\frac{1}{2}; u+\frac{1}{2}, \frac{1}{2}-v, u+\frac{1}{2}.$

Space Group  $O_h^5$ .*Four equivalent positions*4b. 000;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .4c.  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ; 000;  $0\frac{1}{2}0$ ;  $\frac{1}{2}00$ .*Eight equivalent positions*8e.  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .*Twenty-four equivalent positions*24c.  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}\frac{1}{2}0$ ;  $0\frac{1}{2}\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ ; $\frac{1}{2}0\frac{1}{2}$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .24a. u00;  $\bar{u}00$ ; 0u0;  $u+\frac{1}{2}, \frac{1}{2}, 0$ ;  $\frac{1}{2}-u, \frac{1}{2}, 0$ ;  $\frac{1}{2}, u+\frac{1}{2}, 0$ ;  $\frac{1}{2}, \frac{1}{2}-u, 0$ ;  $\frac{1}{2}\frac{1}{2}u$ ;0 $\bar{u}0$ ; 00u; 00 $\bar{u}$ ;  $u+\frac{1}{2}, 0, \frac{1}{2}$ ;  $\frac{1}{2}-u, 0, \frac{1}{2}$ ;  $\frac{1}{2}, 0, u+\frac{1}{2}$ ;  $\frac{1}{2}, 0, \frac{1}{2}-u$ ;  $\frac{1}{2}\frac{1}{2}\bar{u}$ ; $\frac{1}{2}u\frac{1}{2}$ ;  $\frac{1}{2}\bar{u}\frac{1}{2}$ ;  $u\frac{1}{2}\frac{1}{2}$ ;  $0, u+\frac{1}{2}, \frac{1}{2}$ ;  $0, \frac{1}{2}-u, \frac{1}{2}$ ;  $0, \frac{1}{2}, u+\frac{1}{2}$ ;  $0, \frac{1}{2}, \frac{1}{2}-u$ ;  $\bar{u}\frac{1}{2}\frac{1}{2}$ .*Thirty-two equivalent positions*32a. uuu;  $u+\frac{1}{2}, u+\frac{1}{2}, u$ ;  $u+\frac{1}{2}, u, u+\frac{1}{2}$ ;  $u, u+\frac{1}{2}, u+\frac{1}{2}$ ; $\bar{u}\bar{u}\bar{u}$ ;  $u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}$ ;  $u+\frac{1}{2}, \bar{u}, \frac{1}{2}-u$ ;  $u, \frac{1}{2}-u, \frac{1}{2}-u$ ; $\bar{u}u\bar{u}$ ;  $\frac{1}{2}-u, u+\frac{1}{2}, \bar{u}$ ;  $\frac{1}{2}-u, u, \frac{1}{2}-u$ ;  $\bar{u}, u+\frac{1}{2}, \frac{1}{2}-u$ ; $\bar{u}\bar{u}\bar{u}$ ;  $\frac{1}{2}-u, \frac{1}{2}-u, \bar{u}$ ;  $\frac{1}{2}-u, \bar{u}, \frac{1}{2}-u$ ;  $\bar{u}, \frac{1}{2}-u, \frac{1}{2}-u$ ; $\bar{u}uu$ ;  $\frac{1}{2}-u, u+\frac{1}{2}, u$ ;  $\frac{1}{2}-u, u, u+\frac{1}{2}$ ;  $\bar{u}, u+\frac{1}{2}, u+\frac{1}{2}$ ; $u\bar{u}u$ ;  $u+\frac{1}{2}, \frac{1}{2}-u, u$ ;  $u+\frac{1}{2}, \bar{u}, u+\frac{1}{2}$ ;  $u, \frac{1}{2}-u, u+\frac{1}{2}$ ; $uu\bar{u}$ ;  $u+\frac{1}{2}, u+\frac{1}{2}, \bar{u}$ ;  $u+\frac{1}{2}, u, \frac{1}{2}-u$ ;  $u, u+\frac{1}{2}, \frac{1}{2}-u$ .

If 3 of the platinum atoms are alike and different from the fourth platinum atom, then it would be anticipated from the chemical composition of the salt that 6 of the ammonium groups and 18 of the chlorine atoms would be alike but different in some manner from, respectively, the other 2 ammonium groups and the other 6 chlorine atoms (which would be alike among themselves). The space group  $O_h^1$  has no special case having 18 equivalent positions within the unit. Furthermore, suitable special cases do not exist for assuming, for instance, that all of the hydrogen atoms in an ammonium group are not alike or that some of the chlorine atoms about the platinum atoms are different from others, while still maintaining a "three group alike and one group different" arrangement to correspond with the platinum atoms. As a consequence any arrangement of the atoms of ammonium chloroplatinate based upon this space group  $O_h^1$  seems thoroughly improbable from the standpoint of its chemistry. Considered, however, solely as a geometrical problem there are ways of arranging the requisite number of atoms within the unit cell. They are as follows. Possible arrangement (a): *platinum* atoms, 1a or 1b, and 3a or 3b; *chlorine* atoms, 2 of the arrangements having 12 equivalent positions, or 3 sets of the 8 equivalent positions obtained by assigning 3 different values to u, or 4 sets of 6 equivalent positions obtained in a similar manner; *nitrogen* atoms, 8 equivalent positions obtained by assigning some value to u of 8c; *hydrogen* atoms, 4 sets of 8 equivalent positions obtained by assigning 4 different values to the u of 8c, or 2 sets of the 12 equivalent positions and one of the 8 equivalent positions, or 4 different sets of 6 equivalent positions and one of 8 equivalent positions, etc.

It has already been pointed out that if all 4 of the platinum atoms are alike the arrangement of the atoms must be that of either  $O_h^4$  or of  $O_h^5$ . There is every reason to believe that all 4 of the hydrogen atoms in the ammonium radical are chemically identical.<sup>9</sup> If this is correct then these hydrogen atoms by the very definition of their likeness have neighboring atoms arranged in the same way about each. Since in neither of these space groups are there more than 2 special cases having 4 equivalent positions within the unit and since one of these two special cases must be taken up by the platinum atoms, it follows that all 8 of the nitrogen atoms must be alike. Then if the 4 hydrogen atoms of the ammonium group are taken as alike, there must be 32 equivalent hydrogen atoms within the unit cell. This is possible only with the space group  $O_h^5$ . It may consequently be concluded, if the chemical nature of ammonium chloroplatinate is taken into account, that its symmetry is that of the space group  $O_h^5$ .

Two types of ways of arranging the atoms of ammonium chloroplatinate according to the special cases of this space group,  $O_h^5$ , exist. They are as follows. Possible arrangement (b): *platinum* atoms, 4b or 4c; *chlorine* atoms, 24a; *nitrogen* atoms, 8e; *hydrogen* atoms, 32a. Possible arrangement (c): *platinum* atoms, 4b or 4c; *chlorine* atoms, 24c; *nitrogen* atoms, 8e; *hydrogen* atoms, 32a.

In any grouping developed from  $O_h^5$ , a study of its special cases will show that all of the chlorine atoms must be alike and equally distant from a platinum atom. From the chemical nature of ammonium chloroplatinate, again, it is evident that the chlorine atoms are more tightly bound to the platinum atoms than to the ammonium radicals; and according to any reasonable law of force between atoms this would indicate that the chlorine atoms should be nearer to the platinum atoms than to the nitrogen atoms. In arrangement (c) the chlorine atoms lie closer to the nitrogen atoms than to the platinum atoms so that once more employing chemical evidence it can be stated with a considerable degree of probability that the arrangement of the atoms in ammonium chloroplatinate crystals *must* be that defined by arrangement (b).<sup>10</sup>

If this sort of chemical evidence is ignored there are a considerable

<sup>9</sup> For instance the fact that different but isomeric compounds obtained by substituting different organic radicals in place of the hydrogens of ammonium are not obtained seems to point conclusively in this direction.

<sup>10</sup> This discussion has not taken into account the idea of atomic spheres of influence of definite size (W. L. Bragg, *Phil. Mag.*, [6] 40, 169 (1920)). Upon this basis also the chlorine atoms should be nearer to the platinum than to the nitrogen atoms, if the radius of the platinum atom is taken from the recent determination of the structure of the metal (A. W. Hull, *Phys. Rev.*, 17, 571 (1921)) and if the dimensions of the ammonium group are obtained from measurements made on ammonium chloride (W. H. and W. L. Bragg, "X-rays and Crystal Structure," Bell and Sons, London, 1918, p. 111).

number of different ways in which the requisite number of atoms of platinum, nitrogen, chlorine and hydrogen can be grouped within unit cells, and with the existing lack of precise knowledge concerning the laws of scattering it would be a practically hopeless task to try to eliminate them absolutely upon the basis of their predicted diffraction effects. These other possible arrangements would be developed from the space group  $O_h^4$  and would be of the following type. Possible arrangement (d): *platinum* atoms, 4d or 4e; *chlorine* atoms, one set of 24 equivalent positions, or 2 sets of 12 equivalent positions, or 3 sets of 8 equivalent positions, or one set of 12, one of 8 and one of 4 equivalent positions, or arrangements developed by putting 6e and 2a in place of any of the above sets of 8 equivalent positions; *nitrogen* atoms, 8d; *hydrogen* atoms, one set of 24 and 8d, or one set of 24 equivalent positions, 6e and 2a, or 2 sets of 12 or 3 sets of 8 in place of one set of 24 equivalent positions in either of the above, or 4 sets of 8 equivalent positions.

II. Assuming that  $m = 32$ ,  $n = 2$ . If this is the correct amount of mass to be associated with the unit cube, each unit must contain 32 platinum atoms, 64 nitrogen atoms, 192 chlorine atoms and 256 hydrogen atoms. If all 4 of the hydrogen atoms in ammonium are alike it is impossible to associate 32 molecules with the unit cell (unless it be assumed that some of the platinum atoms are different from others) because the maximum number of equivalent positions within the unit cell of any space group is 192. If, however, it is allowed that some of the hydrogen atoms in ammonium may be different from others, then a considerable number of geometrically possible, though chemically far from understandable, groupings can be developed. A consideration of Table IV shows that 3 space groups,  $O_h^5$ ,  $O_h^7$  and  $O_h^8$ , possess special cases with 32 equivalent positions within the unit cube. Two of these, the first two, also show as many as 192 equivalent positions within the unit cell. From either of these if all chemical evidence is disregarded, and in fact from  $O_h^8$  also, it would be possible to build up very complicated arrangements for the atoms of ammonium chloroplatinate. To eliminate with certainty these groupings by a comparison of the diffraction effects which they would produce with those found by experiment is practically impossible in the present state of our knowledge. Since, in the light of chemical evidence, they are at least highly improbable, they will be omitted from further consideration.

**Distinguishing between the Possible Arrangements.**—By making the single assumption that all of the 4 hydrogen atoms of the ammonium radical are chemically exactly alike, it has been shown that the atoms of ammonium chloroplatinate must be placed either according to arrangement (b) or arrangement (c). Of these two, one of them, (c), can be ruled out upon similar grounds. It is, however, possible to distinguish between these two arrangements from the difference in the diffraction effects which

they will produce, so that it is perhaps worth while, if only for purposes of illustration, to show by this instance the method of picking out diffraction effects which will be characteristic of different crystallographically possible arrangements and thus by investigating these characteristic effects to choose the correct grouping.

Calculations of terms proportional to the intensity of reflection from any plane ( $hkl$ ) in any order,  $n$ , of the spectrum have been made by means of an expression of the form

$$I \propto f(d/n) \sum_r [\sigma_r \cos 2\pi n(hx_r + ky_r + lz_r)]^2 + \sum_r [\sigma_r \sin 2\pi n(hx_r + ky_r + lz_r)]^2 \quad (4)$$

where  $I$  is the intensity of reflection,  $f(d/n)$  is a function of the spacing between like planes whose form is not known with great certainty (for the present it does not enter into this discussion), and  $\sigma_r$ , the scattering power of the atom  $r$  for X-rays, seems to be roughly proportional to the atomic number. The summation is to be taken to cover each of the atoms within the unit cube. For convenience in writing  $A$  will be written for the summation of the cosine terms (not squared) and  $B$  for the summation of the corresponding sine terms. This expression (4) would be written  $I \propto f(d/n)[A^2 + B^2]$ .

Applied to the different kinds of atoms of arrangements (b) and (c) this expression gives terms for the intensity of reflection from any plane as follows.

#### Platinum atoms

4b. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , where  $m$ ,  $p$  and  $q$  are any integers (indices=one even, two odd), then  $A=0$ ; the similar sine term,  $B=0$ , also; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$  (two even, one odd indices), then,  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$  (all odd indices), then,  $A=4Pt$ ;  $B=0$ . 4c. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=-4Pt$ ,  $B=0$ .

#### Nitrogen atoms

8e. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ .

#### Chlorine atoms

24c. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ .

24a. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=Cl[8 \cos 2\pi u(2m+1) + 8 \cos 2\pi u(2p+1) + 8 \cos 2\pi u(2q+1)]$ ,  $B=0$ .

*Hydrogen atoms*

The term for the hydrogen atoms will not be taken into consideration for, since the scattering power of an atom of hydrogen is so slight, the effect even of 3 such atoms can scarcely be qualitatively observed.

The value of (4) for arrangements (b) and (c) can be written directly by combining the terms for each of the atomic positions. When  $n=1$  they thus become (neglecting the hydrogen terms).

Arrangement (b): when the indices are either 2 even and 1 odd or 2 odd and 1 even,  $A=0$ ,  $B=0$ ; when the indices are all odd,  $A=\pm 4Pt+8Cl[\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu]$ ,  $B=0$ ;.....(5)

Arrangement (c): except when the indices are all odd  $A=0$ ,  $B=0$ ; then  $A=\pm 4Pt$ ,  $B=0$ . ....(6)

When  $n=2$ : all terms will have appreciable values in the second order so that in dealing with such qualitative measures of diffraction as are now available, discussion will be limited to the first-order region.

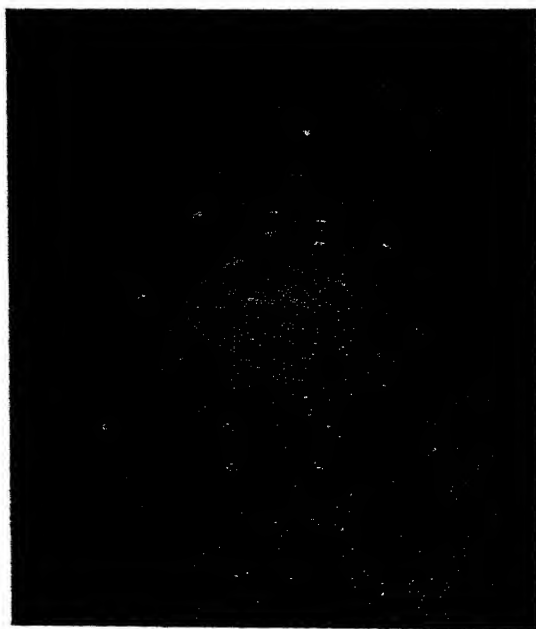


Fig. 2.—A print of the Laue photograph obtained by passing the X-rays in a direction roughly normal to the (111) face of ammonium chloroplatinate.

It is evident that for either (b) or (c) only planes all of whose indices are odd will give first order reflections. Both are in agreement with the results of the reflection spectrum photograph. The most satisfactory way of assuring the correctness of one or the other of these two possibil-

ities and of deciding between them lies then in considering the reflections in the first order from a large number of planes. This is most satisfactorily done at the present time by the study of Laue photographs. This same study should give as well an indication of the position of the chlorine atoms. Their location cannot now be expected with great accuracy without an excessive amount of labor because (1) the hydrogen atoms, though present in a considerable number and hence of quantitative importance, are as already suggested qualitatively insignificant, and (2) because the scattering power of platinum is so great compared with that of chlorine that small changes in the position of the chlorine atoms would be likewise qualitatively of small account. As soon as these reflections can be satisfactorily treated in a quantitative fashion this placing of the chlorine atoms should be easily made.

Two Laue photographs were studied in detail by the customary methods. One, taken normal to the (111) plane, showed reflections from about 400

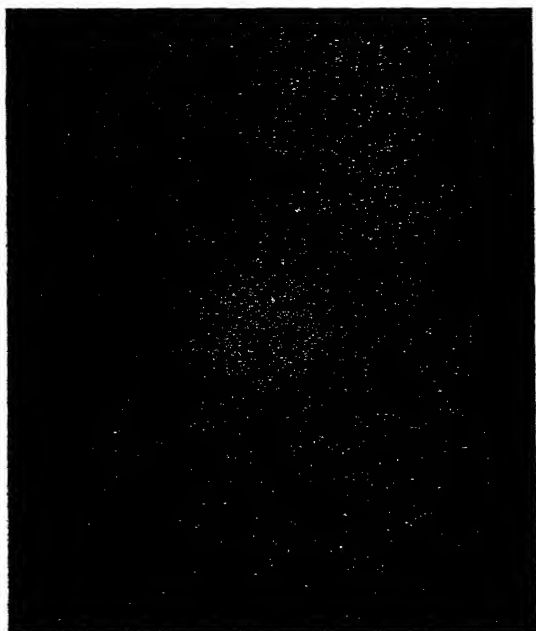


Fig. 3.—A print of the Laue photograph obtained by passing the X-rays in a direction roughly normal to the (100) face of ammonium chloroplatinate.

planes (Fig. 2); the other, tilted somewhat from a normal to the cube plane, contained about 200 spots (Fig. 3). The gnomonic projections of these two photographs are shown in Figs. 4 and 5. By enlarging by the amount shown in the first two figures, these projections will duplicate

the conditions of the original experiment so that from them can be obtained all of the data now available from these photographs. A rough measure of the intensities of the spots is given by the size of the spots in the central reproduction of the photograph, the most intense spots being made the largest. The reproductions of the original photographs (Figs. 2 and 3) are added to make possible slightly more accurate estimations of the intensities of the brighter spots (the only ones that show). A spot can be identified with the projection of its plane in the usual manner, most conveniently by using some such ruler as that already described; and its distance from the central spot and the indices of its reflecting plane can be

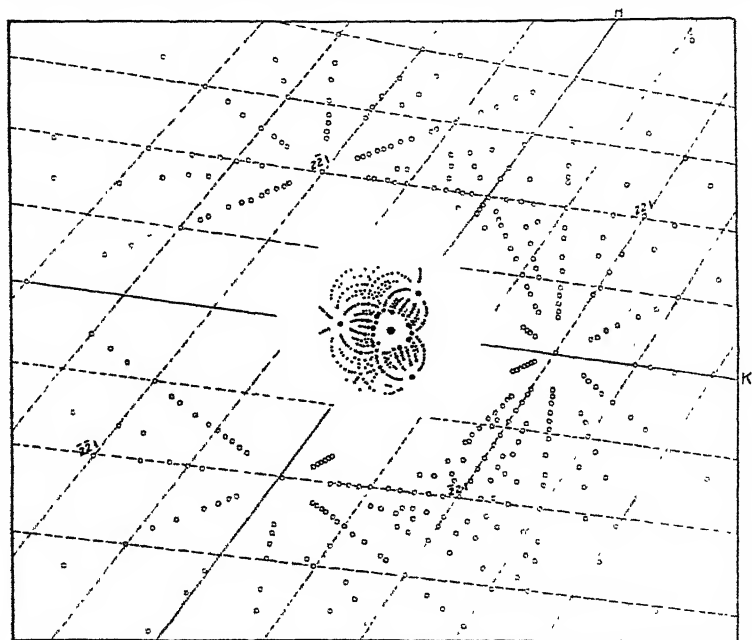


Fig. 4.—The gnomonic projection of the Laue photograph of Fig. 2. Reduced.

directly obtained from measurement upon the central reproduction and upon the projection respectively.<sup>11</sup> The angle  $\theta$  of the reflection can be calculated for any spot from a knowledge of the distance from the crystal to the

<sup>11</sup> It would not be feasible to record the measurements upon approximately 600 planes together with the calculations of the wave lengths producing the spots and their estimated intensities. The inclusion of this mass of data would give an utterly false impression of their present value. Rather than leave out all results, however, the condensed description outlined in the text has been used. In spite of its obvious disadvantages it is possible with such reproductions as are shown here to record in a short space all of these data in such a form that those sufficiently interested can work them out with an approximation to the original accuracy.



photographic plate (which in both of these cases was 5 cm.) and from a measurement of the distance of the spot from the undiffracted image. Combined with a knowledge of the indices of the reflecting plane and by using Expression 2 and the equation  $n\lambda = 2d \sin \theta$ , this evaluation of  $\theta$  makes possible the determination of  $n\lambda$  for each spot.

In neither of these photographs were any spots observed in the first order region (assuming that the number of molecules to be associated with the unit cell is 4 and hence that the reflection observed from the (111) face in the spectrum photograph was of the first order) except those all of whose indices are odd numbers. Some of the indices of these first order

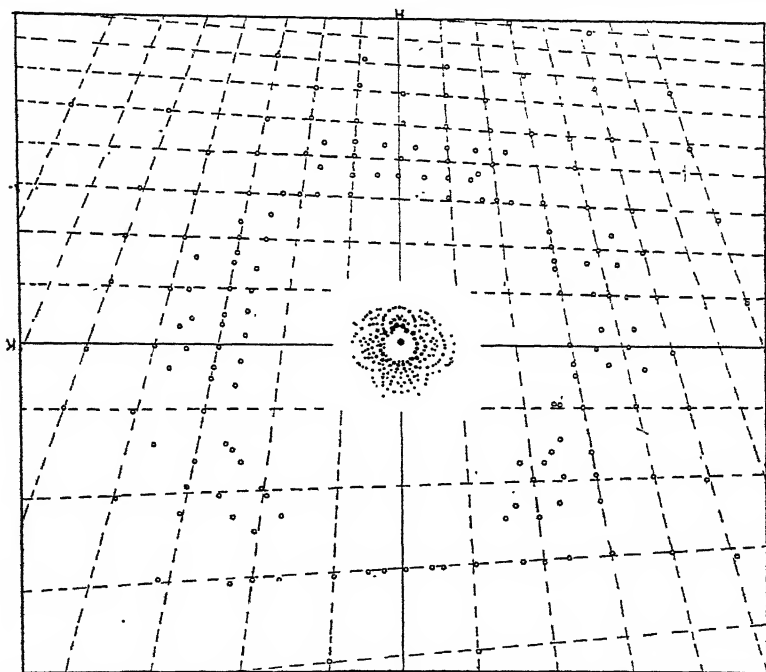


Fig. 5.—The gnomonic projection of the Laue photograph of Fig. 3. Reduced.

planes are such complicated ones as  $(\bar{9} \ 11 \ 5)$  or  $(5 \ \bar{13} \ 3)$  so that the complete absence of any but all-odd planes leaves no doubt as to the truth of the general statement that only planes having all odd indices are found in the first order region. This observation is very strong evidence for the correctness of either arrangement (b) or arrangement (c).

The terms proportional to the amplitude (square root of the intensity) of the first order reflections from arrangements (b) and (c) have been shown to be arrangement (c),  $A = 4Pt$ ; arrangement (b), with the platinum atoms at 4b,  $A_{4b} = 4Pt + 8Cl[\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu]$ ; with the platinum atoms at 4c,  $A_{4c} = -Pt + 8Cl[\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu]$ . But  $A_{4c} =$

$-A_{4b}$  if  $u_{4c}=u_{4b} + \frac{1}{2}$  so that it will be sufficient to discuss but one case (the one involving  $4b$  will be chosen).

It is customary to assume that  $f(d_{hkl}/n)$  in Equation 4 has the form of  $(d_{hkl}/n)^2$ . If this is true and if the atoms are arranged according to (c) then the intensity of the first order reflections from the different planes ( $hkl$ ), at the same wave lengths, should stand in the order of the value of  $1/(h^2 + k^2 + l^2)$ . If, on the other hand, the chlorine atoms have the arrangement (b), this order of intensities will be inverted in part by reason of the term which these chlorine atoms contribute towards the amplitude. Such irregularities are found in the results from the Laue photographs and this may be taken to show that the correct arrangement is that of (b).<sup>12</sup>

A more detailed discussion of such reflections should give an indication of the value of  $u$  for the chlorine atoms. From the results of the study of the Laue photographs, for instance, the following comparisons of the intensity of reflection of waves of practically the same length from different planes are possible

$$\begin{aligned}(173) &< (171) \text{ (by a small amount),} \\ (171) &< (191), \\ (751) &< (171), \\ (751) &< (191) \text{ (by a considerable amount).}\end{aligned}$$

The positions of the chlorine atoms are defined by  $u$  which must consequently be assigned such a value that the above experimental facts must be accounted for when the value of  $(h^2 + k^2 + l^2)$  is taken into consideration (a qualitative ordering of the intensity of the reflections on the basis of this  $f(d/n)$  factor is sufficient). This  $u$  is most readily found by plotting it for each of these planes (Fig. 6) against the corresponding amplitude of reflection as determined through the intensity Equation 5. It is obvious from the form of arrangement 24a that the function will be symmetrical about  $u=0.5$  so that it is sufficient to consider  $u$  from  $u=0$  to  $u=0.5$ . The data given here allow two possible positions for the chlorine atoms, one about  $u=0.1$ , the other close to  $u=0.225$  (Fig. 6). The first of these seems improbable because it would bring the centers of the chlorine and platinum atoms nearer together than is to be anticipated; no data were found, however, definitely to rule out this possibility. If the second position is the correct one the value for  $u$  must lie between  $u=0.22$  and  $u=0.24$ .

It is of interest to calculate, using the idea of closely packed atomic spheres,<sup>13</sup> the expected distance of the chlorine from the platinum atoms

<sup>12</sup> Variations from the normal decline of intensity with increasing values of  $(h^2 + k^2 + l^2)$ , though of but slight amount, would be produced in (c) by the hydrogen atoms. The observed effects seem to be much greater, however, than would be expected from the introduction of this factor into the intensity equation for (c).

<sup>13</sup> W. L. Bragg, *Phil. Mag.*, [6] 40, 169 (1920).

and to compare this distance with the results of the above determination. The radius of the platinum atom, as calculated from the structure of platinum metal<sup>14</sup> is  $1.39 \times 10^{-8}$  cm. To chlorine has been assigned the radius  $1.05 \times 10^{-8}$  cm.<sup>13</sup> Upon this basis then the distance from chlorine to platinum should be  $2.44 \times 10^{-8}$  cm. Taking  $u=0.23$  and knowing the length of the unit cube to be  $9.843 \times 10^{-8}$  cm., this distance is  $2.26 \times 10^{-8}$  cm. (If  $u=0.24$ , it is  $2.36 \times 10^{-8}$  cm.)

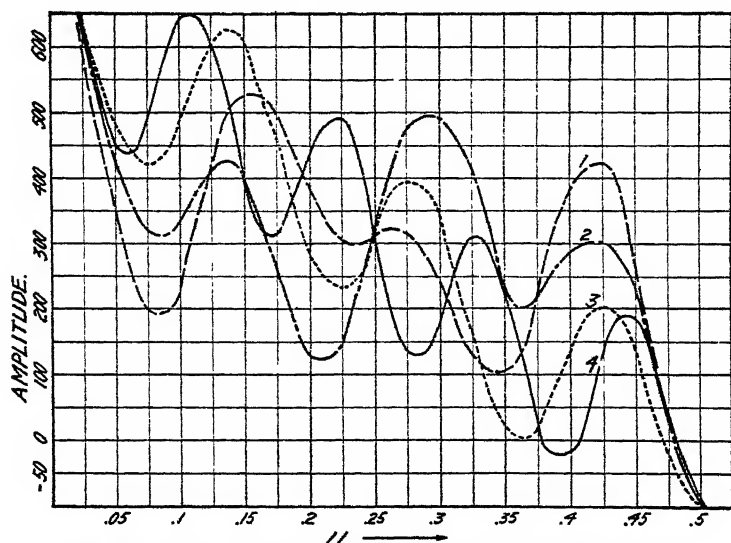


Fig. 6.—Curve 1 = planes of the form (571); Curve 2 = (173); Curve 3 = (171); Curve 4 = (191).

As soon as careful measurements of intensity become possible and satisfactory knowledge of the nature of scattering is available, the more accurate placing of the chlorine atoms in ammonium chloroplatinate and a comparison between their positions in this compound and in other chloroplatinates, as well as a comparison of the structures of these crystals with the analogous fluosilicates, chlorostannates, bromoplatinates, etc., will be easily accomplished and will be of considerable interest.

**Conclusion.**—Making use of the single assumption, which seems to be itself entirely justified, that the 4 hydrogen atoms in the ammonium group are all chemically alike, it has been shown that the atoms in the unit cube of ammonium chloroplatinate have the following coordinate positions: *platinum* atoms, 4b; *chlorine* atoms, 24a, the value of  $u$  probably lying between  $u=0.22$  and  $u=0.24$ ; *nitrogen* atoms, 8c; *hydrogen* atoms, 32a, the value of  $u_H$  being unknown. The length of the side of this unit cube is  $9.843 \times 10^{-8}$  cm. The arrangement of its atoms is shown in Fig.

<sup>14</sup> A. W. Hull, *Phys. Rev.*, **17**, 571 (1921).

7: Fig. 7a shows the positions of only the platinum and nitrogen atoms within a unit cell; Fig. 7b gives the arrangement of all of the atoms within a small cube which has one-eighth of the volume (and one-half the length of side) of this unit.

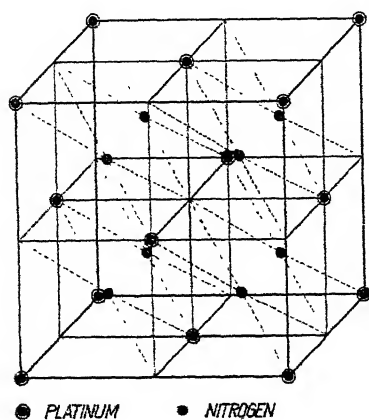


Fig. 7a.

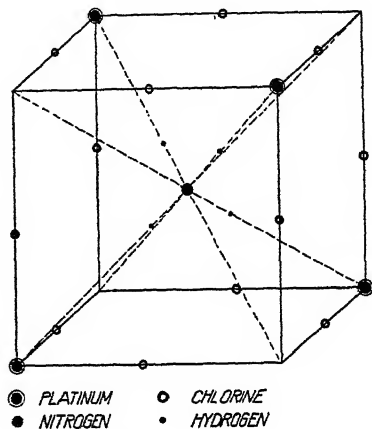


Fig. 7b.

The arrangement of the atoms within the unit cell of ammonium chloroplatinate. Fig. 7a shows the positions of the platinum and nitrogen atoms within the unit; Fig. 7b gives the positions of all of the atoms within the small cube that has one-eighth of the volume of the unit.

**The Chemical Significance of this Crystal Structure.**—This crystal structure of ammonium chloroplatinate is most easily described by saying that it is the same as that of fluorspar ( $\text{CaF}_2$ ) if for the bivalent positive calcium atoms bivalent negative  $\text{PtCl}_6$  groups are substituted and if the monovalent fluorine atoms are replaced by monovalent ammonium radicals. There can be no doubt but that  $\text{PtCl}_6$  groups of atoms function in solution as doubly (negatively) charged ions and that the ammonium radicals under the same conditions are singly charged (positively). Since their crystallization is a strictly analogous process to the crystallization of such salts as the alkali halides, for which there is considerable evidence that the atoms remain ions (that is, remain electrically charged) in the solid state, it is natural to assume that very probably there exists within the crystal of ammonium chloroplatinate the ions of  $\text{PtCl}_6$  and of  $\text{NH}_4$ . The fact that the corresponding compound calcium fluoride  $\text{CaF}_2$ , which from the chemical nature of its elements is presumably also an "ion" compound, has an analogous structure, would seem to indicate that this arrangement is the most stable, or at least is an exceedingly stable, way of grouping one doubly charged and two singly charged (of opposite sign to the doubly charged) atoms or groups of atoms in the crystalline state.

### Summary.

Crystals of ammonium chloroplatinate  $((\text{NH}_4)_2\text{PtCl}_6)$  probably have a structure which is analogous to that commonly assumed for fluor spar, if  $\text{PtCl}_6$  groups replace the calcium atoms and if  $\text{NH}_4$  groups are introduced in place of the fluorine atoms. This determination was made by and serves as an illustration of the general method (previously discussed) for the study of the structure of crystals which is based upon the theory of space groups.

The only assumption made that is not required in the ordinary determination of the wave length of X-rays from a reflection spectrum was that the 4 hydrogen atoms of the ammonium radical are exactly alike; with this exception, that in attempting to place the chlorine atoms with accuracy, it was assumed that atoms scatter X-rays in an amount which is roughly proportional to their atomic numbers and that in a lattice arrangement of atoms the intensities of reflection follow qualitatively the order of  $1/(h^2 + k^2 + l^2)$ .

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### A DIFFERENTIAL THERMOMETER.

BY ALAN W. C. MENZIES.

Received July 2, 1921.

One type of differential thermometer measures the difference of temperature existing at the same location at different times; a second type measures the difference in temperature existing simultaneously at different points in space. The thermometer here described is of the latter type.

A well-known differential thermoscope of this type consists of two glass bulbs containing air, otherwise closed but communicating with each other through a U-tube partly filled with oil, whose change of level indicates change of temperature by responding to change of gas pressure within the bulbs. When this instrument is developed into a differential thermometer, certain disadvantages become apparent, of which three will here be mentioned. (1) When the manometric liquid is caused to run into one of the bulbs by accidental tilting, perhaps during transportation, then it is difficult to return the liquid into precisely the same position as it occupied when the instrument was scaled. If stopcocks are introduced in the effort to avoid this inconvenience, the cure may become worse than the disease i. e. use of zero-creep. (2) In the presence of permanent gas, the manometric liquid becomes, in practice, not infrequently broken into threads, separated by short columns of the gas. This inconvenience, albeit only temporary, is nevertheless annoying. (3) Although oils furnish very sensitive manometric liquids, their use, or, indeed, the use of any liquid

other than the insensitive mercury, allows the entrance of an error that has been too little appreciated. The incidence of this error in tensimetric work has been pointed out by the writer in another connection.<sup>1</sup> The error in question is caused by the fact that a gas at higher pressure has a larger weight solubility than the same gas at a lower pressure. The permanent gas, always slightly soluble in manometric liquids other than mercury, therefore passes by a process of solution and diffusion from the side of higher to that of lower pressure. For this reason, even stopcock-free instruments of the kind referred to suffer from slow creep of the zero point.

In order to avoid these and other disadvantages, all that is necessary is to abandon entirely the use of permanent gas. One selects as manometric



Fig. 1

fluid not oil but some liquid whose change of vapor pressure per degree in the range of temperature where the differential measurements are to be made is such as to cause differences of pressure in the two bulbs of the thermometer that will register themselves by adequate differences of level of the fluid itself. The diagram, Fig. 1, shows one simple form useful in ebullioscopy, made from glass tubing a few millimeters in bore and having, without its handle, a length of perhaps 12 cm. Permanent gas is removed prior to sealing by the process of boiling out familiar to many who have had occasion to measure vapor pressures. For reading the difference of level of the two liquid surfaces a millimeter scale may be etched on both limbs.

From what has been said, it will be clear that, if the environment of both limbs of the instrument is the same in temperature, then the difference of level of the ends of the column of filling liquid will be merely that due to capillarity. If, however, the temperature of the lower bulb in Fig. 1, for example, be higher than that of the other limb, the consequent difference of pressure of vapor in the two limbs will cause in the liquid a correlative change of level whose value may be used, with the help of a suitable table, as a measure of the difference of temperature that caused it.

It is obvious that the sensitiveness in any particular range of temperature may be given widely different values according to the rate of change of vapor pressure of the liquid selected. The difference of temperature between upper and lower bulbs that will cause a change of level of, say, 1 mm. in the height of the column of the filling liquid may be computed from the known vapor pressures and densities of this liquid, and the results tabulated against the mean temperature of the instrument. Because of its suitability in other applications, and particularly because water is a filling liquid well adapted for use in these thermometers as employed in ordinary ebullioscopy, to be described in the article following, a table of precisely

<sup>1</sup> Menzies, *THIS JOURNAL*, 42, 1951 (1920).

the kind indicated is here furnished for a water-filled thermometer. The values for difference of pressure with temperature were obtained from the recent equation of Marvin,<sup>2</sup> which incorporates the best modern values, partly by direct differentiation and partly by the methods of interpolation. Against each tenth of a degree from 33° to 101.9° is tabulated the fraction of a degree centigrade that corresponds to an observed change of level of 1 mm. of water at this temperature. It may be noted that it is unnecessary at each observation to read the levels in both limbs, for the levels in the lower bulb that correspond to readings on the stem may be determined once for all, and the relationship graphed. The fact that such a graph should move parallel to itself as the total volume of contained water increases with temperature is immaterial when differential readings only are required, all close to the same temperature.

TABLE I.

Against each tenth of a degree from 33.0° to 101.9° is entered the change of temperature in ° C that would correspond to a vapor pressure change of water of 1 mm. head of water at the same temperature.

° C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Diff.
33	0.03449	3433	3417	3400	3384	3367	3351	3334	3317	3301	16
34	0.03286	3270	3254	3238	3222	3207	3192	3177	3161	3146	16
35	0.03130	3116	3101	3086	3071	3056	3041	3026	3011	2997	15
36	0.02984	2969	2955	2941	2927	2913	2899	2885	2872	2858	14
37	0.02844	2831	2818	2805	2791	2778	2765	2751	2738	2726	13
38	0.02713	2700	2687	2675	2663	2650	2637	2625	2613	2600	12
39	0.02588	2576	2564	2552	2540	2528	2517	2505	2494	2482	12
40	0.02471	2459	2447	2436	2425	2414	2403	2392	2381	2370	11
41	0.02359	2348	2338	2328	2317	2307	2296	2285	2275	2264	11
42	0.02254	2244	2233	2223	2213	2203	2193	2183	2173	2163	10
43	0.02154	2144	2134	2124	2114	2105	2096	2086	2077	2068	10
44	0.02059	2049	2040	2031	2022	2013	2004	1995	1986	1977	9
45	0.01969	1960	1951	1943	1934	1926	1917	1908	1900	1891	9
46	0.01883	1875	1866	1858	1850	1842	1834	1826	1818	1810	8
47	0.01802	1794	1786	1778	1770	1763	1755	1748	1740	1732	8
48	0.01725	1717	1710	1702	1694	1687	1680	1673	1665	1658	7
49	0.01651	1644	1637	1630	1623	1616	1609	1602	1595	1588	7
50	0.01581	1575	1568	1561	1554	1548	1542	1535	1529	1522	7
51	0.01516	1510	1503	1496	1490	1484	1478	1472	1466	1459	6
52	0.01453	1447	1441	1435	1429	1423	1417	1411	1405	1399	6
53	0.01393	1388	1382	1376	1370	1364	1358	1353	1348	1342	6
54	0.01336	1330	1325	1319	1314	1308	1303	1298	1292	1287	6
55	0.01281	1276	1271	1266	1261	1255	1250	1245	1240	1235	5
56	0.01230	1225	1220	1215	1210	1205	1200	1195	1190	1185	5
57	0.01180	1175	1170	1166	1161	1156	1152	1148	1143	1138	5
58	0.01133	1128	1124	1119	1115	1110	1106	1102	1097	1092	4
59	0.01087	1083	1079	1075	1071	1067	1063	1058	1054	1049	4
60	0.01045	1041	1037	1033	1029	1025	1021	1017	1013	1009	4
61	0.001005	1001	9968	9928	9890	9851	9813	9772	9734	9696	
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	

<sup>2</sup> Cf. Menzies, *THIS JOURNAL*, 43, 852 (1921).

TABLE I (*Continued*).

°C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Diff.
62	0.009658	9620	9583	9545	9508	9470	9432	9396	9359	9322	37
63	0.009285	9249	9212	9177	9141	9105	9069	9034	8999	8963	35
64	0.008931	8896	8861	8826	8792	8758	8725	8692	8658	8624	34
65	0.008592	8559	8527	8494	8461	8428	8397	8365	8333	8301	32
66	0.008269	8237	8207	8175	8145	8114	8083	8052	8022	7991	31
67	0.007960	7930	7900	7870	7840	7810	7780	7750	7721	7691	30
68	0.007663	7633	7605	7575	7548	7519	7491	7463	7435	7406	29
69	0.007379	7352	7324	7297	7269	7242	7214	7188	7161	7135	27
70	0.007109	7083	7057	7031	7005	6979	6953	6928	6902	6877	26
71	0.006852	6826	6801	6776	6751	6727	6702	6677	6653	6629	25
72	0.006606	6582	6557	6533	6509	6485	6462	6439	6415	6392	24
73	0.006369	6346	6323	6301	6277	6255	6232	6210	6187	6165	23
74	0.006144	6121	6099	6077	6055	6033	6011	5989	5969	5947	22
75	0.005927	5906	5884	5863	5842	5822	5801	5781	5760	5740	21
76	0.005719	5698	5676	5657	5637	5618	5598	5578	5558	5539	20
77	0.005520	5499	5480	5461	5442	5423	5404	5384	5365	5347	19
78	0.005328	5310	5291	5273	5254	5236	5218	5200	5182	5163	18
79	0.005145	5127	5109	5091	5074	5056	5039	5021	5003	4986	18
80	0.004969	4952	4935	4918	4901	4884	4867	4851	4834	4817	17
81	0.004800	4784	4767	4751	4735	4719	4702	4686	4670	4654	16
82	0.004638	4623	4607	4592	4576	4560	4545	4530	4514	4499	15
83	0.004484	4469	4453	4438	4423	4408	4393	4378	4363	4349	15
84	0.004334	4319	4305	4290	4276	4262	4248	4234	4220	4206	14
85	0.004192	4178	4165	4151	4137	4124	4111	4097	4083	4069	14
86	0.004055	4042	4029	4016	4002	3989	3976	3963	3950	3937	13
87	0.003923	3910	3897	3885	3873	3860	3847	3834	3821	3809	13
88	0.003796	3784	3771	3759	3747	3735	3723	3711	3698	3686	12
89	0.003675	3663	3651	3639	3627	3616	3604	3592	3581	3569	12
90	0.003557	3546	3535	3524	3513	3500	3488	3477	3465	3454	11
91	0.003443	3433	3422	3410	3399	3388	3378	3367	3356	3345	11
92	0.003334	3323	3313	3302	3292	3281	3271	3260	3249	3239	10
93	0.003229	3219	3209	3200	3189	3179	3169	3159	3149	3138	10
94	0.003128	3118	3109	3099	3089	3080	3070	3060	3051	3041	10
95	0.003032	3022	3013	3004	2994	2985	2976	2967	2957	2948	9
96	0.002939	2930	2921	2912	2903	2894	2885	2876	2867	2858	9
97	0.002849	2841	2832	2823	2815	2806	2798	2789	2781	2772	9
98	0.002764	2755	2747	2738	2730	2722	2713	2705	2697	2689	8
99	0.002680	2672	2664	2656	2647	2639	2631	2623	2615	2607	8
100	0.002599	2592	2584	2576	2568	2561	2554	2546	2538	2530	8
101	0.002523	2516	2508	2501	2494	2486	2478	2471	2463	2456	7
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	

Although the thermometers are of different general types, as indicated above, it is of interest to compare this differential thermometer with the Cavendish-Walferdin<sup>3</sup> metastatic type as elaborated by Beckmann,<sup>4</sup> and as applied in the same field, for example that of ebullioscopy. With regard to length of scale per degree, the Beckmann mercurial type is

<sup>3</sup> Cavendish, *Trans. Roy. Soc. London*, 50, 300 (1757). Walferdin, *Bull. soc. géol. France*, 13, 113 (1841-2).

<sup>4</sup> Beckmann, *Z. physik. Chem.*, 2, 644 (1888); 51, 329 (1905).



limited by the usable size of bulb, and by the permissible narrowness of the capillary, so that a centigrade degree corresponds customarily to 40 or 50 mm. movement of the mercurial thread. The type here described is not thus limited in this respect, for a very low-boiling liquid may be used for filling. In both types the length of degree varies with the actual temperature. As to range, the Beckmann type is restricted to that between  $-39^{\circ}$  and  $+250^{\circ}$ .<sup>5</sup> While this is a much larger range than can be conveniently covered by the use of a single chosen liquid in the newer type, the simplicity of construction makes possible such a wide choice of filling liquids that a much wider range is easily available in the direction of lower as well as of higher temperatures. In comparing precision, one has to bear in mind, for the Beckmann type, possibilities of error due to (1) lack of uniformity of bore, (2) hysteresis in change of volume of bulb, (3) effect of pressure on volume of bulb, (4) sticking of mercury in capillary, (5) exposed thread, (6) difference of radiation to and from bulb, (7) departure of apparent degree from true degree. For the type here described, no one of the first six of these sources of error is important, for reasons that will be sufficiently obvious. In regard to (6), it may perhaps be said that error due to the change with environment of radiation loss suffered by a Beckmann thermometer at temperatures far from room temperature is here largely eliminated because suffered alike by upper and lower bulb. With regard to (7), it is indeed most necessary to employ a factor, different for each temperature, to convert observed readings to temperature; and this factor may be criticized as inconvenient to use, inaccurate in value and laborious of computation. But the use of a similar factor is likewise necessary, although frequently neglected, in the case of the Beckmann thermometer, whose degree, if true at  $0^{\circ}$ , is, for example, about 3% in error at  $80^{\circ}$ .<sup>6</sup> The accuracy of the conversion factor for the newer type is dependent in part on the accuracy with which the vapor pressure of the filling liquid is known. For such liquids as would be employed, and within the ranges of temperature that come in question here, this quantity, the vapor pressure, can now be measured to better than one part in 1000.<sup>7</sup> The process of computing factors for, perhaps, each tenth part of a degree over a considerable range of temperature may indeed be laborious; but, once published, the factor table may be used by every one. This inconvenience, therefore, is shifted from the shoulders of the user of the thermometer to those of him who first computed the table.

The Beckmann type is considerably more cumbersome as well as very much more fragile than the type here described, which one constructs from stout

<sup>5</sup> Cf. Staehler, "Arbeitsmethoden in der Anorg. Chemie," Veit and Co., Leipzig, 1913, part 3, vol. 1, i, p. 106.

<sup>6</sup> Staehler, *op. cit.*, p. 108.

<sup>7</sup> Cf. *THIS JOURNAL*, 32, 1412 (1910).

walled Pyrex tubing. In connection with fragility, it may be added that no "setting" of the thermometer for different temperatures is required, for its zero reading for uniform temperature automatically adjusts itself near the bottom of the stem, thus leaving the major portion of the scale available throughout its whole length.

In certain respects, therefore, it would appear that this type of differential thermometer has advantages over the Walferdin metastatic type as elaborated by Beckmann; and the question arises as to whether such other factors as are peculiar to a given application are favorable to its use. In studying its application in ebullioscopy, for example, as outlined in the article following, one finds that the important disturbing factor, peculiar to ebullioscopy in its incidence, of barometric fluctuation does not measurably affect the readings of the newer type, while such pressure fluctuations are among the chief outstanding sources of error when the metastatic type is used. Another application in a different field may be described in the near future.

#### Summary.

A very simple form of differential thermometer has been described whose indications depend on the registration by a column of manometric liquid in a U-tube of differences of vapor pressure of this liquid in opposite limbs. A table is given for use when the filling liquid is water; and mention is made of certain advantages of this type over the metastatic type of thermometer.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY.]

### THE APPLICATION OF A DIFFERENTIAL THERMOMETER IN EBULLIOSCOPY.

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Received July 2, 1921.

For purposes of molecular weight determination of dissolved substances, the ebullioscopic procedure has certain advantages over the method of cryoscopy. Since, to use the latter, one must for convenience employ solvents whose freezing points lie at easily accessible temperatures, it comes about that water, benzene and acetic acid have been commonly preferred. To obtain satisfactory values for the molecular weight of a solute, it is best to choose a solvent so like it chemically that compound formation shall be at a minimum. To be so closely restricted in the choice of solvents is therefore a disadvantage. Boiling temperatures are, in general, preferable to freezing temperatures as unfavorable to the formation of exothermic compounds. A majority of organic compounds boil normally below 300°. If, as is true, the solvent should differ by at least 150 degrees in boiling point from the solute in order that the volatility of the latter may

not vitiate the results, then, for most practical purposes, the use is indicated of such solvents as boil rather below  $100^{\circ}$  than above it, and these solvents are in point of fact those most commonly used. The low solubility of certain solutes at the freezing points of the available solvents is a factor against cryoscopy. On the other hand, the precision attainable in cryoscopy has, in the past, been considerably greater than that realized in ebullioscopy, even with apparatus fortified against error by the superimposition of a multiplicity of paraphernalia.

For these and other reasons, a very great deal of work has been carried out by very many investigators with a view to improving the ebullioscopic technique. One may but mention the two dozen papers by Beckmann and his collaborators;<sup>1</sup> and the work of Hite,<sup>2</sup> Orndorff and Cameron,<sup>3</sup> Jones,<sup>4</sup> Ross Innes,<sup>5</sup> Meyer and Desamari,<sup>6</sup> Drucker,<sup>7</sup> Sakurai,<sup>8</sup> Landsberger,<sup>9</sup> Walker and Lumsden,<sup>10</sup> McCoy,<sup>11</sup> Smits,<sup>12</sup> Rijber,<sup>13</sup> Ludlam,<sup>14</sup> Erdmann and Unruh,<sup>15</sup> Lehner,<sup>16</sup> and Turner.<sup>17</sup> Even a single publication by one writer, Hite, reports the trial of over 100 different forms of apparatus. In all these, and many other investigations, the bulb of a mercurial thermometer has been submerged beneath the surface of the boiling solution, and much of the work has been directed to the avoidance of the consequent irregular superheating. In our opinion, the two most successful improvements made since 1892 have originated in this country, the introduction, namely, by Bigelow<sup>18</sup> of electric heating, and by Cottrell<sup>19</sup> of a "lift-pump" which pumps the solution over the bulb of the thermometer, which no

<sup>1</sup> References to the numerous papers of Beckmann and his collaborators may be found in the work of Jellinek, "Lehrbuch der Physikalischen Chemie," 2, 783 *et seq.*, (1915); and also in Staehler's "Handbuch der Arbeitsmethoden in der Anorg. Chemie," 3, i (1913).

<sup>2</sup> Hite, *Am. Chem. J.*, 17, 514 (1895).

<sup>3</sup> Orndorff and Cameron, *ibid.*, 17, 517 (1895).

<sup>4</sup> Jones, "The Freezing-Point, Boiling-Point and Conductivity Methods," Chemical Publishing Co., Easton, Pa., 1912.

<sup>5</sup> Ross Innes, *J. Chem. Soc.*, 81, 682 (1902).

<sup>6</sup> Meyer and Desamari, *Ber.*, 42, 797 (1909).

<sup>7</sup> Drucker, *Z. physik. Chem.*, 74, 612 (1910).

<sup>8</sup> Sakurai, *J. Chem. Soc.*, 61, 989 (1892).

<sup>9</sup> Landsberger, *Ber.*, 31, 461 (1898).

<sup>10</sup> Walker and Lumsden, *J. Chem. Soc.*, 73, 502 (1898).

<sup>11</sup> McCoy, *Am. Chem. J.*, 23, 502 (1900).

<sup>12</sup> Smits, *Proc. Acad. Sci. Amsterdam*, 3, 86 (1900).

<sup>13</sup> Rijber, *Ber.*, 34, 1060 (1901).

<sup>14</sup> Ludlam, *J. Chem. Soc.*, 81, 1193 (1902).

<sup>15</sup> Erdmann and Unruh, *Z. anorg. Chem.*, 32, 413 (1902).

<sup>16</sup> Lehner, *Ber.*, 36, 1104 (1903).

<sup>17</sup> Turner, *J. Chem. Soc.*, 97, 1104 (1910).

<sup>18</sup> Bigelow, *Am. Chem. J.*, 22, 280 (1899).

<sup>19</sup> Cottrell, *THIS JOURNAL*, 41, 721 (1919).

longer need be submerged in the solution, but is located above the solution in the vapor phase. When Cottrell's device is employed, there remain outstanding, for non-volatile solutes, the errors inherent in the use of the Beckmann type of thermometer, the error due to uncertainty as to actual concentration of solute, and the very troublesome error due to change of boiling point caused by change of barometric pressure during the observations.<sup>20</sup> This last may, in part at least, be overcome by the employment of somewhat cumbersome "manostats,"<sup>21</sup> by especially constructed aneroid barometers,<sup>22</sup> or by the use of a second, duplicate, apparatus<sup>23</sup> operated simultaneously and containing another Beckmann thermometer immersed in the pure boiling solvent.

In 1910, Menzies<sup>24</sup> had described a simple apparatus, independent of barometric change, which, when properly constructed, gives molecular weights of solutes in solvents at their boiling points by direct measurement of lowering of vapor pressure, without the use of any thermometer. Continuing this effort at simplification, he found that the differential thermometer of the preceding article,<sup>25</sup> when applied to ebullioscopy with the Beckmann type of apparatus, served only to render more glaring the inevitable irregularities inseparable from that method of procedure. When however, Cottrell's paper appeared in 1919, opportunity was taken to work out the simplest possible apparatus and technique which should free ebullioscopy from all its most serious drawbacks.

**The Apparatus.**—The diagram, Fig. 1, shows a boiling tube, whose narrowed upper portion itself serves as condenser tube. A glass cylinder, open above and below and of diameter slightly less than the boiling tube, is located concentrically within the latter, and confers the advantages of a double jacket. Within this is supported the differential thermometer, on the lower bulb of which hangs the pump, loosely, as a hat on a peg.<sup>26</sup> The absence of rigid connection diminishes possibility of breakage, besides adding flexibility, literal and metaphorical.<sup>27</sup> The boiling tube is heated

<sup>20</sup> Cf. Meyer and Desamari, *Ber.*, 42, 2809 (1909), who were misled by this error into obtaining only one-half the true value for the molecular weight of tribromo-resoquinone, and so to assigning to it an inaccurate formula. The practical text-books often recommend postponing ebullioscopy to a day when the barometer is steady.

<sup>21</sup> Cf. Smits, *Z. physik. Chem.*, 39, 415 (1902); Burt, *J. Chem. Soc.*, 85, 339 (1904); Drucker, *Ref. 7.*; Beckmann, *Z. physik. Chem.*, 79, 565 (1912); etc.

<sup>22</sup> Meyer and Desamari, *Ber.*, 42, 797 (1909).

<sup>23</sup> Cf. Beckmann, *Ref. 1.*; Washburn and Read, *THIS JOURNAL*, 41, 729 (1919); Sluiter, *Proc. Acad. Sci. Amsterdam*, 17, 1043 (1914).

<sup>24</sup> Menzies, *THIS JOURNAL*, 32, 1615 (1910).

<sup>25</sup> Menzies, *ibid.*, 43, 2309 (1921).

<sup>26</sup> The complete apparatus, with both boiling tube and water-filled thermometer of Pyrex glass, is furnished by Messrs Eimer and Amend, 205 Third Avenue, New York, N. Y.

<sup>27</sup> We have on no occasion yet broken any part of the apparatus.

by direct contact with the low flame of a common Bunsen burner, protected by the customary draughtshield of metal, best in an inverted position. When boiling begins, portions of the liquid in the bulb are carried by the vapor in fragments up the pump and discharged to form a thin film over the lower bulb of the thermometer, which thus attains the temperature at which this liquid, or solution, is in equilibrium with the vapor. The upper bulb acquires the temperature of the pure boiling solvent. The thermometer registers the difference between these two temperatures. Equilibrium is reached so rapidly, except in cases of slow solubility, that fresh additions of solute may be made as fast as they can be weighed out. Contrary to all ebullioscopic tradition, the apparatus will give good results in a room that is not free from draughts. Unlike every other ebullioscopic apparatus, this form is entirely free from all corks, ground glass joints or stoppers.

The sources of error, including that due to barometric change, eliminated by the use of the new type of differential thermometer have been briefly referred to in the preceding article. The advantages gained by removing the lower bulb from immersion in the boiling liquid have been well explained by Cottrell,<sup>19</sup> and confirmed by Washburn and Read<sup>23</sup> and by Spencer,<sup>28</sup> to whose interesting papers the reader is referred for consideration of many matters that cannot be dealt with here. To their remarks may, perhaps, be added that the error due to change of bubble size caused by the marked change of surface tension on addition of certain solutes; that due to change of head of liquid above the thermometer bulb; and the errors caused by fractionation of the solvent and by slow removal by distillation of somewhat volatile solutes, incident to the Sakurai-Landsberger method, are also alike avoided. The chief residual source of error lies in the uncertainty as to the true concentration of the boiling solution as deduced, not by subsequent analysis, but simply from the weights of solvent and solute used. Part of the solvent is absent from the solution in the form of condensate on the walls, and part is absent in the form of vapor. This source of error, ever present in the Beckmann type of apparatus, has often failed of due consideration. To minimize it, we constrict the boiling tube above the lower bulb, mark cc. graduations on the cylindrical neck so developed, and read off the actual working volume of the solvent an instant after ebullition has been caused to cease, while the tube is still wet with condensate and filled with vapor.

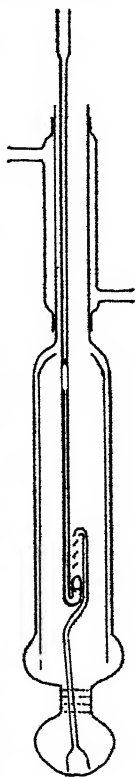


Fig. 1.

<sup>28</sup> Spencer, *THIS JOURNAL*, 43, 301 (1921).

A simple water-filled differential thermometer suffices for the range of temperature from the boiling point of water to that of ether, thus embracing the use of such solvents as carbon disulfide, acetone, chloroform, methyl, ethyl and propyl alcohols, methyl acetate and iodide, ethyl formate, acetate, bromide and iodide; carbon tetrachloride, and benzene, and allowing a choice adequate for ordinary purposes. No "setting" of the thermometer is required for the use of different liquids.

**Method of Procedure.**—The boiling tube is clamped in a vertical position by means of a large single clamp located just under the upper side-tube of the condenser jacket. Beneath it is clamped a Bunsen burner at such a height that when the top of its tube is in position about 1 cm. below the bottom of the boiling tube, the base of the burner is a few centimeters above the sole of the supporting ring-stand. The boiling tube is filled with solvent to the level of the lower graduations on the constricted neck, the condenser water turned on, and the flame lighted and suitably adjusted by means of the customary screw-clip. The boiling point of the solvent is now taken to the nearest tenth of a degree by means of a good ordinary thermometer, in which operation the avoidance of exposed thread is usually easy. While the thermometer used for this purpose is reaching thermal equilibrium, the barometer may conveniently be read, and information thus obtained as to the purity of the solvent. The actual working volume of the solvent is next found by lowering the burner (not its gas supply) so that it is ready to be swung clear, quickly swinging it aside, and causing instant cessation of bubble formation by immersing the bottom of the boiling tube in cold water raised by hand from below in a small beaker. The reading of volume—best against a white card in the background—should be made immediately ebullition is caused to cease, before the access of solvent that drains from the walls. The burner is then replaced in position. For purposes of molecular-weight determination, one may employ as ebullioscopic constant the boiling-point rise in degree produced by one mole of solute per 100 cc. of solvent at its boiling point ( $K_2$  in Table I p. 2320). The mercurial thermometer is now withdrawn, the pump introduced and lowered to the bottom of the boiling tube by means of a deep hook on the end of a wire, and the differential thermometer inserted, engaged on the pump, and clamped in suitable position by the end of its handle which is made wide so as to be more easily gripped by the clamp. While temperature equilibrium is being reached, which may occupy 15 minutes, it is convenient to prepare pastilles of the solute and to make the first weighing of the bottle containing them.

In making readings of the differential thermometer, the error of parallax may be simply avoided by fixing a white card, of the size of a postal card, with bold graduations in centimeters across it corresponding to those on the thermometer, at a suitable distance behind the latter at the same level,

and placing the eye so that the readings on card and thermometer correspond. The zero reading is given by the difference between the readings on the stem and on the lower bulb, and its value obviously serves as a most useful index of the purity of the solvent. Unsteadiness of reading is caused by too slow boiling.

A pastille of solute is now dropped, from forceps, down the condenser. If it be easy of solution, the reading will at once rise and become constant the moment solution is complete. The ebullioscopic rise is obtained by subtraction of the zero reading from the difference of level now observed. This is later translated into temperature at leisure by the help of a conversion factor extracted from such a table as that given in another communication.<sup>25</sup> It is to be noted that, for fine work, in order to obtain the true conversion factor, one must use as argument the average temperature of the two ends of the thermometer, which is higher than the boiling point previously found by the mercurial thermometer by an increment of temperature corresponding to half the observed ebullioscopic rise. If half the ebullioscopic rise multiplied by the factor selected by a first inspection does not, when added to the boiling point of the solvent, yield a temperature that agrees with the chosen factor, then the factor may be reselected accordingly.

**Case of Volatile Solutes.**—It is generally agreed<sup>29</sup> that, for purposes of straightforward molecular weight determination, the boiling point of an ebullioscopic solvent should lie at least 150° below that of the solute. For this reason, benzil (b. p. 347°) has found favor as a standardizing solute because it may be assumed to be virtually absent from the vapors escaping from its solution in the common ebullioscopic solvents. If, however, the solute be as volatile as naphthalene (b. p. 218°) in boiling carbon tetrachloride or benzene, then one would anticipate that the mixed vapors, on partial condensation, would tend to yield a liquid of the concentration with which they are in equilibrium, namely the concentration of the solution from which they have just escaped. The upper bulb of the differential thermometer might thus be expected to acquire precisely the same temperature as the lower bulb; and, if precaution be taken to minimize condensation on the thermometer, this condition can indeed be approximated. The gross composition of the vapor phase, however, is close to that of the pure solvent, so that if this vapor is completely condensed and caused to lave the upper portion of the differential thermometer, the temperature it acquires in contact with the surrounding vapor is very close to the boiling point of the pure solvent, which is the temperature here desired. In order to provide an adequate laving of this kind, a very simple plan is to embrace the handle of the thermometer, at a point a few centimeters above the upper bulb, with a pair of wires of

<sup>29</sup> Cf. Staehler, Ref. 1.

perhaps 24 S.W.G. twisted together where they meet on opposite sides of the handle, and to direct the two twisted tags so formed upwards in such a way that, by resting against the inner walls of the condenser tube, they may uniformly divert a modicum of the condensate on to themselves and thence to the thermometer. The diagram, Fig. 2, shows these wires, which are prevented from slipping either up or down by reason of the slight constriction in the handle where they are applied. In practice

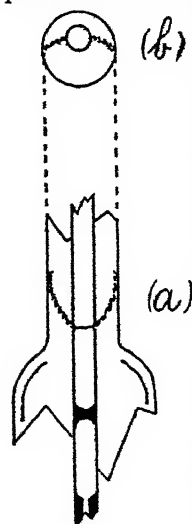


Fig. 2.

it is useful to employ these wires in all cases, not only because of possible prejudicial volatility of the solute, but to meet the contingency of spattering of the upper portion of the thermometer by minute droplets from a frothing solution. The wires may also very conveniently be bent so that the handle of the thermometer is stationed sufficiently eccentrically within the condenser tube as to allow a very clear passage for the introduction of pastilles. This is indicated in Fig. 2 (b).

**Collected Useful Data.**—In Table I are collected, from diverse sources, certain useful data for a few of the commoner solvents: their normal boiling points; the barometric change,  $dp/dt$ , in mm. of mercury that produces a change of  $1^\circ$  in the boiling point; the density,  $D$ , of the liquid at the boiling point; its change,  $dD/dt$ , per degree of temperature; the ebullioscopic constant,  $K_1$ , for one mole of solute in 100 g. of solvent; the ebullioscopic constant,  $K_2$ , for one mole of solute in 100 cc. of solvent at its boiling point.

TABLE I.  
CONSTANTS USEFUL IN EBULLIOSCOPY.

Solvent.	B.p. $^\circ\text{C}$	$dp/dt$ .	$D$ .	$dD/dt$ .	$K_1$ .	$K_2$ .
Acetone.....	57.0	26.4	0.7522	0.0011	17.2	22.9
Benzene.....	80.1	23.4	0.8149	0.0010	26.1	32.0
Carbon disulfide.....	46.3	24.7	1.2223	0.0016	23.7	19.4
Carbon tetrachloride..	76.8	23.3	1.4801	0.0021	48.0	32.4
Chloroform.....	61.2	25.2	1.4101	0.0018	39.0	27.7
Ethyl acetate.....	77.2	25.1	0.8302	0.0010	27.9	33.6
Ethyl alcohol.....	78.4	30.3	0.7389	0.0011	11.7	15.8
Ethyl ether.....	34.6	26.9	0.6968	0.0011	21.6	31.1
Methyl acetate.....	57.1	26.8	0.8802	0.0014	20.6	23.4
Methyl alcohol.....	64.7	29.6	0.7468	0.0010	8.8	11.8

The values for  $K_1$  are taken chiefly from Staehler's *Handbuch*<sup>1</sup> as an impartial source. We doubt the accuracy of some of these values. It must be remembered that the values determined and adopted by even a single investigator such as Beckmann, for example, have varied from time to time. The matter will be reverted to on another occasion. The change



of the ebullioscopic constants with barometric pressure is of the order of 0.3% per 10 mm. near 760 mm.

**Examples of Results.**—We shall here limit ourselves to a very few typical cases to illustrate merely the consistency of the results obtainable by the use of this apparatus, and their general agreement with the results of others. For a later redetermination of certain ebullioscopic constants, especial purification of materials and other precautions will be required; but for the present purpose the ordinary materials of the laboratory supply-room have proved sufficient. In order to conform to the practice of Beckmann and most others, we have employed in computing our results the well-known simple, if inadequate, relationship  $K_1 = \text{temp. rise} \times \text{mol. wt. of solute} \times \text{wt. of solvent} \div 100 \times \text{wt. of solute}$ .

(a). **Benzil in Benzene.**—Values of the ebullioscopic constant  $K_1$  used by Beckmann<sup>30</sup> were 26.7 (1890), 26.1 (1895), 24.2 (1905), 25.7 (1907, 1914). Drucker<sup>7</sup> found 26.7, Innes<sup>5</sup> 24.1, etc. Beckmann's present accepted value, 25.7, is the mean of two sets of each three measurements with benzil in benzene, as follows: (1) rise, 0.180°, 0.354°, 0.568°, corresponding respectively to  $K_1 = 25.7, 25.6, 25.2$ ; (2) rise, 0.205°, 0.450°, 0.688°, yielding  $K_1 = 25.6, 26.2, 25.7$ . We made two sets of

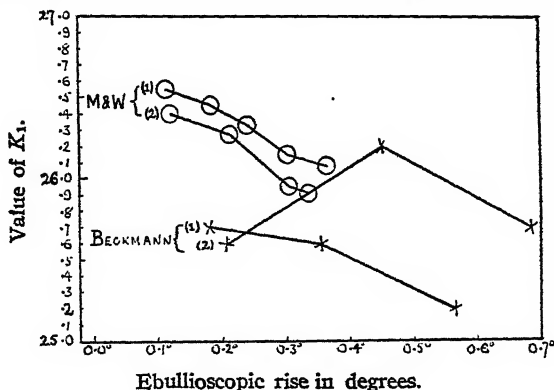


Fig. 3.

measurements, on different days, as follows: (1) rise, 0.1142°, 0.1820°, 0.2440°, 0.3016°, 0.3661°, corresponding respectively to  $K_1 = 26.6, 26.5, 26.3, 26.2, 26.1$ ; (2) rise, 0.1218°, 0.2126°, 0.3052°, 0.3355°, yielding  $K_1 = 26.4, 26.3, 26.0, 25.9$ . The fourth significant figure has some meaning for our higher readings. From these data, which are shown plotted in Fig. 3, it would appear that the values in each of our sets are rather more self-consistent than those of Beckmann, although obtained with much simpler apparatus; and that 0.1 mm. on the scale of the differential thermometer may be estimated successfully. Our two sets differ from each other, on the average by 0.6%, an error that would be caused by an error of 0.2 cc. in reading 30.0 cc., the approximate volume of benzene employed. As we have learned from many other results, this is the largest value to which this error ever attains; more often the error from this cause is 0.1 or 0.0 cc., averaging well under 0.5% in the result. Aside from possible systematic error, it is the chief single source of error entering into our determi-

<sup>30</sup> Cf. Beckmann, *Z. physik. Chem.*, 88, 23 (1914); 58, 555 (1907).

nations. The details of the observations of Set 1 follow, serving to illustrate the use of conversion factor and to indicate the time consumed.

TABLE II.  
OBSERVATIONS OF SET 1.

Volume of benzene at the boiling point, 31.6 cc. Boiling temperature, corrected, 79.7°. Barometric reading, corrected, 755.2 mm. Solute, benzil, 210.1.

Obs. No.	Time. h. m.	Wt. of benzil. G.	Diff. therm. reading. Mm.	Conversion factor.	Rise. °C.	$K_1$ .
0	1.26	0.0	10.5 (zero)	.....	0.0	...
1	1.32	0.2326	22.8 (above zero)	0.005011	0.1142	26.56
2	1.36	0.3726	36.4 (above zero)	0.005005	0.1820	26.46
3	1.41	0.5011	48.8 (above zero)	0.004999	0.2440	26.33
4	1.46	0.6238	60.4 (above zero)	0.004994	0.3016	26.16
5	1.52	0.7595	73.4 (above zero)	0.004988	0.3661	26.08

(b). Anthracene in Chloroform.—Benzol, alcohol and chloroform are perhaps the three best-studied ebullioscopic solvents, and we chose this example because, in particular, the Sakurai-Landsberger method has been critically studied by Turner<sup>17</sup> who used it to redetermine the constant for chloroform. Of Turner's solutes, anthracene was most readily available to us in reasonably pure form.<sup>21</sup> Because of its ease of decomposition, we do not regard chloroform as so suitable an ebullioscopic solvent as carbon tetrachloride, which covers a similar field of solutes.

In the two sets of experiments for which he gives data, Turner obtained the following results: (1) rise, 0.646°, 0.527°, 0.436°, 0.363°, corresponding respectively to  $K_1 = 40.5, 40.4, 40.5, 40.3$ ; (2) rise, 0.559°, 0.455°, 0.376°, yielding  $K_1 = 38.3, 38.0, 38.5$ . In two sets of experiments we obtained, (1) rise, 0.2672°, 0.3981°, 0.5045°, 0.6213°, yielding  $K_1 = 39.58, 39.42, 39.09, 38.66$ ; (2) rise, 0.3166°, 0.4042°, 0.4792°, 0.5565°, 0.6515°, yielding  $K_1 = 39.90, 39.25, 38.56, 38.59, 38.09$ . Turner averages his two sets at 40.4 and 38.3 respectively,—results discrepant by 5.4%, or 2.7% from their mean. Our results, when plotted, diverge from a straight line drawn through them by 0.56% on the average. It may be said that the impure chloroform used does not show our method to advantage. The unsatisfactory character of chloroform as an ebullioscopic solvent is further indicated by the rather wide variation of the values for the constant employed by Beckmann from time to time, ranging from 35.9 (1895) to 39.0 (1908).

(c). Naphthalene in Ether and in Carbon Tetrachloride.—It is necessary to add these further examples to illustrate the use of an appreciably volatile solute. In a single run in which we added 8 successive quantities of naphthalene to ether of normal boiling point, 34.1°, with consequent elevations of temperature ranging from 0.27° to 2.04°, we obtained values for  $K_1$  of 21.47, 21.43, 21.11, 20.68, 20.39, 20.31, 19.82, 19.77, results which diverge on the average by about 0.33% from a straight line drawn through their plot. If, however, the twisted wires described above were omitted in this case, the results obtained were low and unsatisfactory. It should, perhaps, be added that one does not expect strict rectilinearity in the graph obtained as above; and that, in the case of ether, which has a considerable vapor pressure at the temperature of the condenser, a small correction, under 1% per hour, might be made for progressive loss of solvent by diffusion into the air. A straight line, however, is undeniably a smooth curve, for purposes of reference.

Carbon tetrachloride boils only 141° below naphthalene, thus falling within the forbidden range of 150° referred to above. To secure more copious lavage of the upper

<sup>21</sup> Through the courtesy of the Chemical Department of the Barrett Co.

portion of the thermometer by the condensate in this case, we employed twisted double wires instead of single wires in constructing the drainage mechanism, and opened the ends in contact with the condenser tube so as to form forks, thus withdrawing the condensate from the walls at four points each served by a pair of wires twisted together. This had the effect of raising the zero reading by a few millimeters. Using a solvent of normal boiling point,  $76.2^{\circ}$ , we obtained, from elevations of  $0.1888^{\circ}$ ,  $0.2822^{\circ}$  and  $0.3990^{\circ}$ , values for  $K_1$  of 47.23, 47.89, and 48.46. For computation merely the simple relationship mentioned above was utilized, without correction for volatility of the naphthalene. Benzene as solvent for naphthalene gave results of similar quality, thus demonstrating that usable results may still be obtained even in these somewhat adverse cases.

### Summary.

A simple apparatus for ebullioscopy has been described and illustrated in which is employed a new type of differential thermometer. Most of the sources of experimental error that have influenced the very many earlier forms of ebullioscopic apparatus have here been avoided or so minimized that results consistent to within 0.5% are readily obtained.

PRINCETON, NEW JERSEY.

[CONTRIBUTION FROM THE SYNTHETIC PRODUCTS LABORATORY, DRUG DIVISION, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

## DISTRIBUTION OF CERTAIN DRUGS BETWEEN IMMISCIBLE SOLVENTS.

By W. O. EMERY AND C. D. WRIGHT.

Received July 11, 1921.

Of the many medicinal preparations examined by this laboratory, those containing analgesic and antipyretic agents have been fruitful fields for various lines of investigation. In the isolation of these substances preliminary to their quantitative determination, recourse was frequently had to the use of immiscible solvents, such as aqueous solutions and chloroform, the latter preferably on account of its physical properties and consequent ease of separation and recovery. During the earlier stages of the work, the relative volumes of the solvents, as well as the number of extractions deemed necessary or expedient for complete isolation of the substance sought, were governed largely by empirical considerations, care, being taken, however, that any error of commission should involve an excess rather than a deficiency in organic solvent. In operations with caffeine and antipyrine, for example, substances possessing about equal solubility in chloroform but differing widely in this respect toward water (1 g. of caffeine is soluble in 46 mls, 1 g. of antipyrine on the other hand in less than 1 ml of water), it was assumed that, given like volumes, antipyrine would require a greater number of extractions than caffeine. From preliminary experiments on controls, carried out in the usual way with the

Squibb type of separatory funnel at the room temperature, results were obtained quite different from those anticipated. Thus, in "shaking out" caffeine and antipyrine with chloroform, one such treatment effected the following recoveries from aqueous solutions.

TABLE I.  
RECOVERY OF CAFFEINE AND ANTIPYRINE WITH CHLOROFORM.

Subs. in aq. soln. G.	CHCl <sub>3</sub> . Cc.	H <sub>2</sub> O. Cc.	Caffeine. %.	Antipyrine recovery.
0.1000	50	20	98.2	98.0
0.1000	50	20	98.1	—
0.1000	50	20 <sup>a</sup>	97.5	96.0
0.1000	50	20 <sup>b</sup>	97.6	—
0.1000	20	20	94.3	94.0
0.1000	20	50	88.1	88.0
0.2000	50	20	—	97.0
0.5000	50	20	—	97.5
1.0000	50	20	—	96.0

<sup>a</sup>Acidified with H<sub>2</sub>SO<sub>4</sub>.

<sup>b</sup>Made alkaline with NaOH.

These findings seemed to indicate that under more nearly ideal conditions involving moderate to low concentrations the distribution ratios of caffeine and antipyrine between aqueous solutions and chloroform might be almost if not quite, identical. The results as above tabulated formed the material for a preliminary communication to the Society at its 49th (Spring) meeting in Cincinnati, and in effect constituted the main incentive to the present study. Owing to the intervening war, however, and the consequent interruption to the normal activities of the Bureau, the final solution of the problem has involved a period of time far in excess of that originally contemplated.

### Caffeine.

In order to gather more precise information relative to some of the factors influencing distribution, such as temperature, concentration, alcohol, acid, alkali and other solutes, several series of experiments were carried out, at first in a so-called constant temperature room at about 19.5°, later in a water-bath maintained at different temperatures, but accurate to within 1°. The pipet employed in this work for withdrawing the chloroform was specially prepared by drawing out the tip of an ordinary 25cc. instrument to a capillary about 10 cm. in length, and adjusting the volume by blowing a small bulb in the stem to 25.00 ± 0.02 cc., as determined by the weight of water delivered.

**Effect of temperature.**—In these and the following experiments, portions of anhydrous caffeine<sup>1</sup> were weighed out in small glass capsules and placed in glass-stoppered bottles of about 150cc. capacity, and then by means of a pipet prepared as above 50 cc. of water and 50 cc. of chloro-

<sup>1</sup> The caffeine used was a well-known commercial brand, recrystallized from water and dried at 100°.

form were added, the bottles were tightly stoppered and placed in a water-bath at the desired temperature, shaken vigorously at intervals and finally allowed to stand until the water and chloroform layers had become clear. Meanwhile, and in order to forestall any possible intake of the aqueous layer preparatory to withdrawal of the chloroform aliquot a minute bulb was blown at the extreme tip of the pipet, sufficiently thin to be easily crushed by gentle pressure against the bottom of the container, 25 cc. of the chloroform was withdrawn and run into a tared beaker. The solvent was then evaporated by an air blast and gentle heat, and the beaker and contents were weighed. The difference in weight multiplied by two<sup>2</sup> represents the amount of caffeine in the chloroform layer. The results obtained in the first extractions are given below.

TABLE II.  
EFFECT OF TEMPERATURE UPON EXTRACTION WITH CHLOROFORM.

Total caffeine. G.	Temp. °C.	Caffeine in 25 cc. of CHCl <sub>3</sub> . G.	Recovery. %.
0.5000	12	0.2407	96.3
0.5000	21	0.2383	95.3
0.5000	30	0.2357	94.3
0.5000	40	0.2330	93.2

It is evident that a low temperature is favorable to the extraction of caffeine from water by means of chloroform.

**Effect of concentration.**—A series of experiments similar to the above was carried out in the constant-temperature room at about 19.5°, but with varying concentration of caffeine, with the following results.

TABLE III.  
EFFECT OF CONCENTRATION OF CAFFEINE UPON EXTRACTION.

Total caffeine. G.	Caffeine in 25 cc. of CHCl <sub>3</sub> . G.	Recovery. %.
0.1000	0.0480	96.0
0.2000	0.0958	95.8
0.5000	0.2376	95.0
1.0000	0.4702	94.0
2.0000	0.9240	92.4
2.5000	1.1400	91.2
5.0000	2.1710	86.8

The above findings show that the distribution is more favorable to the chloroform in dilute solution, *i. e.*, that the recovery of caffeine decreases with increase in concentration in water.

**Effect of alcohol.**—Since U. S. P. chloroform contains 0.6 to 1.0% of alcohol, it was of interest to determine how much, if at all, distribution

<sup>2</sup> On the assumption that the volume of the chloroform layer is the same as that introduced. This is of course not strictly true, since the caffeine increases the volume slightly. Another conceivable source of error would be in a change in the volumes of water and chloroform on shaking, owing to mutual solubility, but tests indicated that this is inappreciable.

would be influenced by its presence. A similar series of experiments was therefore carried out, using instead of pure chloroform a mixture containing 1% of alcohol, prepared by diluting 5 cc. of absolute alcohol to 500 cc. with chloroform. These experiments were likewise conducted at the uniform temperature of 19.5°.

TABLE IV.

## EFFECT OF ALCOHOL IN CHLOROFORM UPON EXTRACTION OF CAFFEINE.

Total caffeine. G.	Caffeine in 25 cc. of CHCl <sub>3</sub> . G.	Recovery. %.
0.1000	0.0483	96.6
0.2000	0.0964	96.4
0.5000	0.2403	96.1
1.0000	0.4752	95.0
2.5000	1.1500	92.0
5.0000	2.1810	87.2

These percentages are in all probability somewhat too high, due to the fact that most of the alcohol passes into the water on shaking, with consequent diminution of the chloroform layer, the 25cc. portion removed representing slightly more than  $\frac{1}{2}$  of the total volume. A more accurate method would undoubtedly be to use a 1% solution of alcohol in water, and alcohol-free chloroform.

**Effect of Acid.**—The feebly basic character of caffeine makes the study of its extraction from acid solutions of considerable interest. Accordingly, experiments were undertaken to determine its distribution between pure chloroform and *N* sulfuric acid, 50 cc. of each reagent being taken. The temperature in this series was maintained at 20.4°.

TABLE V.

## EFFECT OF ACID SOLUTIONS UPON EXTRACTION OF CAFFEINE.

Total caffeine. G.	Caffeine in 25 cc. of CHCl <sub>3</sub> . G.	Recovery. %.
0.1000	0.0455	91.0
0.2000	0.0908	90.8
0.5000	0.2255	90.2
1.0000	0.4463	89.3
2.5000	1.0795	86.4
5.0000	2.0410	81.6

These results are what might be reasonably expected, showing as they do a somewhat less efficient extraction from an acid solution. Beal and Lewis,<sup>3</sup> on the other hand, operating on 0.2g. samples of caffeine in 25cc. portions of 0.5 *N*, 0.25 *N* and 0.125 *N* sulfuric acid with 20cc. portions of chloroform, report higher recoveries for caffeine than were obtained from a similar operation on a neutral aqueous solution. The accompanying Fig. 1 affords a graphical representation of results obtained in the above three series.

<sup>3</sup> Beal and Lewis, *J. Am. Pharm. Assoc.*, 5, 824 (1916).

**Effect of other solutes.**—The influence of various solutes, as ammonium hydroxide, sodium hydroxide, sodium acetate, sodium salicylate, sucrose, and citric acid, was observed in a few preliminary experiments with the Squibb type of separatory funnel at a temperature of about 25°.

TABLE VI.  
EFFECT OF OTHER SOLUTES UPON EXTRACTION OF CAFFEINE.

Total caffeine. G.	CHCl <sub>3</sub> . Cc.	Cc.	Aqueous solvent.	Recovery. %.
0.5000	25	20	H <sub>2</sub> O + 5 cc. of 28% NH <sub>4</sub> OH	94.1
0.5000	25	20	H <sub>2</sub> O + 5 cc. of 5% NaOH	95.5
0.5000	50	50	mol. Na acetate sol.	96.6
0.5000	25	25	mol. Na salicylate sol.	20.7
0.5000	25	25	0.1 mol. Na salicylate sol.	82.0
0.2000	50	50	mol. sucrose sol.	96.4
0.5000	25	25	mol. citric acid sol.	85.2

Of these and other solutes examined in this manner, sodium salicylate appears to have by far the greatest effect on the distribution ratio, due apparently to the formation of some molecular compound not readily yielding its caffeine component to the chloroform.

**Constant temperature bath.**—In order to control temperature conditions more accurately, a tank was constructed of sheet copper, elliptical in form, with double walls inclosing an insulating space 25 mm. thick, packed with "mineral wool." The inside dimensions were, length 70 cm., width 50 cm. and depth 45 cm., thus affording a capacity of about 150 liters. A tubular vertical shaft at the lower end carried, in addition to a set of stirring blades, a curved cross tube (hydraulic tourniquet or Barker's mill type), and a glass mercury-cup seal at the top similar to that illustrated by Hudson,<sup>4</sup> which, being connected by rubber tubing

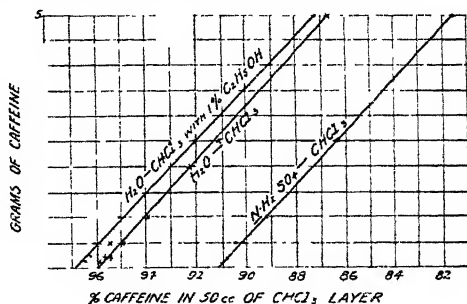


Fig. 1.

with a jacket of glass tubing 38 mm. in diameter containing either a pipet or buret as the experiment required, served as a pump for drawing water from the bath, and thus gave vigorous circulation and maintained the pipet (or buret) with its contents at the same temperature. A temperature control within 0.01° was secured by means of a hydrogen-sealed mercury thermo-regulator of the general type described by Clark,<sup>5</sup> heat being supplied by two 100-watt carbon lamps submerged in the water and controlled by a relay in the usual manner, which served to maintain the bath at 25° when the room was not below 20°, and also to illuminate the interior. In the event of temperatures lower than 20°, additional heat could be supplied by means of an auxiliary resistance coil. The temperature of 25° was selected because of its convenience and close approximation to ordinary laboratory conditions, also because it is the standard of the U. S. Pharmacopeia. For convenient observation

<sup>4</sup> Hudson, *THIS JOURNAL*, 30, 1572 (1908).

<sup>5</sup> Clark, *ibid.*, 35, 1889 (1913).

of the temperature, a Beckmann thermometer was used, the reading corresponding to 25.00° being determined by comparison with two calibrated (Bureau of Standards) thermometers reading to 0.01°. Midway of the tank was a submerged horizontal shaft so geared as to rotate about 20 times per minute, carrying spring clamps suitable for holding bottles. These were of the type known as "German tinctures", having flat-topped glass stoppers. They were very carefully tested for leakage before use. A basket at the side of the tank was provided for allowing the bottles to stand submerged to the necks for any period of time desired.

### Solubility of Caffeine.

In connection with the work on distribution, it was deemed advisable to acquire additional information on the solubility of caffeine in both water and certain aqueous solutions, the more so since the values obtained in some of the earlier experiments were unquestionably too high, due to supersaturation. Considerable difficulty was experienced in overcoming this condition. Starting with anhydrous caffeine, a much larger apparent solubility is obtained, hence it is necessary to convert the substance into its hydrated form by solution and redeposition before a true equilibrium is established. If sufficient caffeine is originally taken, such supersaturated solutions yield a dense mass of hydrated crystals from which no solution can be separated conveniently. The anhydrous form, therefore, has a much greater solubility, but is unstable under these conditions. The method as finally developed for caffeine is essentially that outlined below.

TABLE VII.  
SOLUBILITIES OF CAFFEINE IN VARIOUS AQUEOUS SOLUTIONS.

Solvent.	Caffeine in 10 cc.	
	G. <sup>a</sup>	G.
Water .....	0.2133	0.2072
	0.2199	0.2063
	0.2183	0.2074
	0.2316	0.2076
	mean	0.2071
<i>N</i> sulfuric acid.....	0.3495	0.3361
	0.3526	0.3351
<i>N</i> citric acid.....		0.6406
		0.6417
<i>N</i> potassium bromide.....		0.2135
		0.2137
2.5 <i>N</i> potassium bromide.....		0.2031
		0.2041
<i>N</i> sodium salicylate .....	2.282	2.221
	2.278	2.222
	2.274	2.222
0.1 <i>N</i> sodium salicylate .....		0.4930
		0.4913
<i>N</i> sodium benzoate .....		1.545
		1.527
		1.511
0.1 <i>N</i> sodium benzoate.....		0.3431
		0.3414

<sup>a</sup> These values are unquestionably too high, being the result of earlier operations not strictly in accord with the above method.



**Method.**—Bottles containing the solvent and an excess of caffeine were allowed to stand for 3 days (or until the separation of crystals appeared to be complete), then rotated for 2 hours, and allowed to stand for another 2 hours in the bath. Portions of the clear solution were thereupon withdrawn by means of the water-jacketed pipet referred to above, and, in the case of water, run directly into tared beakers for evaporation, or into separatory funnels for extraction of the caffeine with chloroform from the other aqueous media employed.

The relatively high values obtained in certain of these experiments, notably in the case of sodium salicylate and benzoate, point to the existence of molecular compounds having a higher solubility than caffeine itself. The existence of such compounds has already been assumed by Daudt,<sup>6</sup> but so far as known no satisfactory proof has as yet been adduced.

**Cryoscopic experiments.**—In order to obtain further information on the increased solubility of caffeine in salicylate and benzoate solutions, and on the nature of the combinations existing therein, experiments were undertaken with solutions containing these solutes singly and in admixture, using the ordinary Beckmann freezing-point apparatus. The results obtained are given below, being averages of several determinations.

TABLE VIII.  
FREEZING-POINT DEPRESSIONS.

Solute in 100 cc.	Depression. °C.	
Caffeine, 1 g. ....	0.08	
Sodium salicylate, 1 g. ....	0.23	
Caffeine + sod. salicylate, each, 1 g. ....	0.233	(0.31°) <sup>a</sup>
Sodium salicylate, 0.824 g. <sup>b</sup> ....	0.20	
Caff. 1 g. + sod. salicylate, 0.824 g. ....	0.20	(0.28°) <sup>a</sup>
Sodium benzoate, 0.742 g. <sup>b</sup> ....	0.22	
Caff. 1 g. + sod. benzoate 0.742 g. ....	0.26	(0.30°) <sup>a</sup>

<sup>a</sup> Sums of the depressions of the single solutes.

<sup>b</sup> These amounts represent the molecular equivalent of 1 gram of caffeine.

The above values clearly show that, in the case of sodium salicylate solutions, the addition of a molecular equivalent of caffeine produces no further depression of the freezing point; and, in the case of sodium benzoate solutions, the addition of a molecular equivalent of caffeine produces only about  $\frac{1}{2}$  the depression to be expected. These results are in apparent harmony with those obtained in the solubility tests, and, as will later appear, in the distribution studies.

**Distribution.**—In the experiments on caffeine enumerated below, the chloroform and aqueous solutions were brought to 25° by standing in the constant-temperature bath; then, by means of the jacketed pipets referred to previously, were measured into bottles containing weighed amounts of caffeine, the aqueous layer being introduced first in order to minimize loss by evaporation. The bottles were tightly stoppered and, to insure that they remained so, cork discs were laid over the stoppers and spring clamps applied to hold them firmly in place. After rotating for two hours, and standing for about the same period in the bath as in the case of the solubility experiments, half aliquot portions of the chloroform layer<sup>2</sup> were with-

<sup>6</sup> Daudt, *Pharm. Ztg.*, 32, 376 (1887).

drawn by jacketed capillary-tipped pipets and run into tared beakers for evaporation. In the cases where salts were present, an additional precaution was taken of washing with a small portion of water in a separatory funnel, the chloroform aliquot removed, the water then being exhausted of any dissolved caffeine by two small portions of chloroform, and all of the latter solvent evaporated in a tared beaker. The results obtained in the several series are as follows.

TABLE IX.  
DISTRIBUTION EXPERIMENTS WITH CAFFEINE.

Total caffeine. G.	Aqueous Solvent. Cc.	Chloroform. Cc.	G.	Caffeine recovery. %.
I. Water and absolute chloroform.				
0.1000	50	50	0.0479	95.8
0.2000	50	50	0.0957	95.7
0.5000	50	50	0.2368	94.7
1.0000	50	50	0.4685	93.7
1.0000	20	20	0.4575	91.5
2.0000	20	20	0.866	86.6
1.0000	20	20	0.455	91.0
2.0000	20	20	0.864	86.4
1.0000	20	20	0.457	91.4
2.0000	20	20	0.865	86.5
II. <i>N</i> sulfuric acid and absolute chloroform.				
0.1000	50	50	0.0455	91.0
0.5000	50	50	0.2232	89.3
1.0000	50	50	0.4434	88.7
0.1000	50	50	0.0456	91.2
0.1000	50	50	0.0450	90.0
0.1000	50	50	0.0453	90.6
0.2000	50	50	0.0904	90.4
0.2000	50	50	0.0898	89.8
0.2000	50	50	0.0911	91.1
0.5000	50	50	0.2238	89.5
1.0000	20	20	0.4307	86.1
2.0000	20	20	0.8166	81.7
III. <i>N</i> potassium bromide and absolute chloroform.				
0.1000	50	50	0.0482	96.4
0.1000	50	50	0.0485	97.0
0.1000	50	50	0.0483	96.6
0.2000	50	50	0.0958	95.8
0.2000	50	50	0.0964	96.4
0.2000	50	50	0.0957	95.7
0.2000	50	50	0.0957	95.7
0.5000	50	50	0.2373	94.9
0.5000	50	50	0.2379	95.2
1.0000	50	50	0.4702	94.0
1.0000	50	50	0.4709	94.2
1.0000	20	20	0.4567	91.3
2.0000	20	20	0.8671	86.7

TABLE IX (continued).

Total caffeine. G.	Aqueous Solvent. Cc.	Chloroform. Cc.	Caffeine recovery. G.	%.
IV. 0.1 N sodium salicylate and absolute chloroform.				
0.1000	50	50	0.0427	85.4
0.2000	50	50	0.0848	84.8
0.5000	50	50	0.2094	83.8
1.0000	50	50	0.4147	82.9
0.1000	50	50	0.0426	85.2
1.0000	20	20	0.4021	80.4
2.0000	20	20	0.7641	76.4
1.0000	20	20	0.4012	80.2
2.0000	20	20	0.7615	76.2
2.0000	20	20	0.7644	76.4
V. 0.1 N sodium benzoate and absolute chloroform.				
0.1000	50	50	0.0466	93.2
0.2000	50	50	0.0922	92.2
0.5000	50	50	0.2238	91.5
1.0000	50	50	0.4532	90.6
1.0000	20	20	0.4375	87.5
2.0000	20	20	0.8249	82.5
0.1000	50	50	0.0466	93.2
0.1000	50	50	0.0459	91.8
0.2000	50	50	0.0926	92.6

A graphical representation of these data is given in Fig. 2.

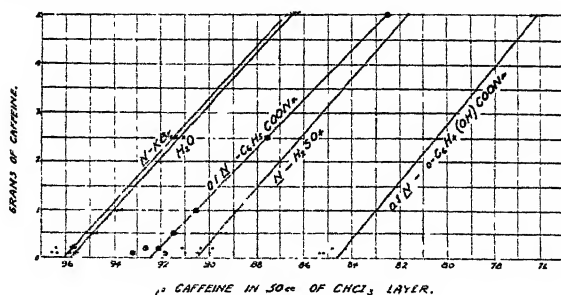


Fig. 2.

from which the relatively slight effect of potassium bromide, as contrasted with that of the other solutes, is immediately apparent. Since the percentage error in the case of small amounts of caffeine is naturally much greater than when larger quantities are employed, the exact course of the line at such low concentrations becomes difficult of determination.

### Antipyrine.

The procedure followed in studying the distribution of antipyrine between absolute chloroform and aqueous solutions was in the main quite similar to that described for caffeine, with this difference, however, that instead of weighing the recovered product directly the residues obtained

on evaporation of the chloroform half-aliquots, which are withdrawn after rotation in the constant-temperature bath, were titrated either as a whole (in alcoholic solution with iodine in the presence of mercuric chloride), or as aliquots, according to the method of Bougault.<sup>7</sup> As a preliminary thereto, a few tests were carried out in Squibb separatory funnels at 25° with U. S. P. chloroform and aqueous solutions of sodium acetate, potassium bromide, sucrose and sulfuric acid. The results obtained in these operations are indicated below.

TABLE X.  
CHLOROFORM EXTRACTION OF ANTIPYRINE.  
50 cc. of chloroform used in each experiment.

Total antipyrine. G.	Aqueous solvent.	Recovery. %.
0.1000	50 cc. mol. Na acetate	95.6
0.1000	50 cc. mol. K bromide	95.9
0.2000	50 cc. mol. sucrose	95.8
0.1000	50 cc. $N H_2SO_4$	54.2

The values yielded by the use of bottle containers in connection with the constant temperature bath are given in the following series.

TABLE XI.  
DISTRIBUTION EXPERIMENTS WITH ANTIPYRINE.

Total antipyrine. G.	Aqueous solvent. Cc.	Chloroform. Cc.	Antipyrine by titration. G.	%.
VI. Water and absolute chloroform.				
0.1000	50	50	0.0481	96.2
0.2000	50	50	0.0959	95.9
0.5000	50	50	0.2368	94.7
1.0000	50	50	0.4698	94.0
1.0000	20	20	0.4605	92.1
2.0000	20	20	0.884	88.4
VII. $N$ sulfuric acid and absolute chloroform.				
0.1000	50	50	0.0273	54.6
0.2000	50	50	0.0529	52.9
0.5000	50	50	0.1339	53.6
1.0000	50	50	0.2662	53.2
1.0000	20	20	0.2685	53.7
2.0000	20	20	0.5432	54.3
2.0000	20	20	0.5426	54.3
0.5000	50	50	0.1341	53.6
VIII. 0.1 $N$ sodium salicylate and absolute chloroform.				
0.1000	50	50	0.0477	95.4
0.2000	50	50	0.0947	94.7
2.0000	20	20	0.8760	87.5
0.5000	50	50	0.2354	94.2
1.0000	20	20	0.4584	91.7
1.0000	20	20	0.4576	91.5
0.1000	50	50	0.0477	95.4
1.0000	50	50	0.4672	93.4

<sup>7</sup> Bougault, *J. Pharm. chim.*, 1, 858 (1898).

Fig. 3 is a graphical representation of the results shown in the last three series.

A study of these data shows that there is no such tendency to the formation of double salts as obtains in the case of caffeine (cf. Series IV and VIII). There is, on the other hand, a far greater depression in the percentage of antipyrine extracted from *N* sulfuric acid, when compared with that from purely aqueous solution, due presumably to difference in basicity.

### *p*-Acetoxy-acetanilide.

As a preliminary to more refined work on the behavior of this substance when agitated with water and U. S. P. chloroform, a few experiments were

carried out in the usual way with separatory funnels at a temperature of about 20°. The material employed in this and all subsequent work was a carefully recrystallized product melting at 150–151°. The results obtained as also the quantities of solute and solvents involved, are indicated below.

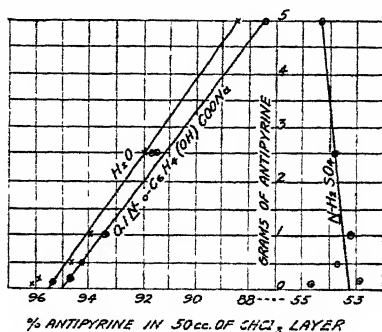


Fig. 3.

TABLE XII.

RECOVERY OF <i>p</i> -ACETOXY-ACETANILIDE.				
Total solute. G.	Water. Cc.	Chloroform. Cc.	Recovery in 1st ext'n.	
			G.	%.
0.1000	25	25	0.0891	89.1
0.1000	25	25	0.0891	89.1
0.1000	10	25	0.0953	95.3
0.1000	25	10	0.0776	77.6

These results reflect a somewhat lower distribution ratio than obtains for either caffeine or antipyrine under like treatment.

**Solubility.**—Preparatory to a more exact study on distribution, some information was deemed essential with respect to the solubility of *p*-acetoxy-acetanilide, notably in water and absolute chloroform. The method followed in this case was quite similar to that described under caffeine, with the exception that the bottles containing the solvent and excess of solute were rotated immediately upon receipt of their respective charges at 25° in the constant-temperature bath. The amounts of solute found in these experiments were as follows.

SOLUBILITY OF <i>p</i> -ACETOXY-ACETANILIDE.		—Solute in 10 cc.
Solvent.		G.
Water.....		0.0237
		0.0238
		0.0240
	mean	0.0239
		0.3250
Chloroform.....		0.3251
		0.3248
		0.3248
	mean	0.3250



negligible amount of the solute in question, as also in calculating the percentage of substance originally present in solution from data yielded by the first extraction. However attractive in principle these procedures may appear, it must be equally apparent to anyone skilled in the art that their general adoption could yield satisfactory results only under the most ideal conditions. In their practical application to many of the problems peculiar to drug analysis, one would certainly encounter grave difficulties, as in the formation of emulsions of greater or less persistence, which prevent any sharp separation of the two liquid media, more particularly, however, in cases involving two or more solutes and the possible existence of molecular compounds, which, as has been noted in the work above described, markedly affect the distribution.

### Summary.

1. Studies have been made of the effect of temperature and concentration on the distribution of caffeine between water and chloroform.
2. The effect of the presence of other solutes in the aqueous layer on distribution has been determined at 25°.
3. The solubility of caffeine in water and certain aqueous solutions has been measured at 25°.
4. Further proof of the existence of molecular compounds of caffeine with sodium salicylate and sodium benzoate in aqueous solution has been obtained by cryoscopic measurements.
5. The distribution of antipyrine has been determined under similar conditions.
6. The solubility of *p*-acetoxy-acetanilide in water and chloroform has been measured at 25°. Its distribution between water and chloroform has likewise been determined.
7. Comparison of the distribution curves for caffeine and antipyrine between water and chloroform confirms the earlier assumption that the distribution ratios of these substances are nearly if not quite identical.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

## THE HEAT OF COAGULATION OF FERRIC OXIDE HYDROSOL WITH ELECTROLYTES.<sup>1</sup>

BY FREDERICK L. BROWNE AND J. HOWARD MATHEWS.

Received July 15, 1921.

### Introduction.

The pioneers in the field of colloid chemistry, for example Selmi,<sup>2</sup> Graham,<sup>3</sup> and Linder and Picton,<sup>4</sup> attached great significance to the fact that they found no measurable change in temperature accompanying the formation or the coagulation of colloidal dispersions. The formation of a true solution always involves a heat change which it has been customary by way of loose illustrative analogy to regard as being similar in nature to the thermal effect involved in the change of state of a pure substance. In passing into solution, the solid absorbs the analogs of the heats of fusion and of vaporization in order to attain a condition which in many ways resembles that of a gas. In addition there frequently are other phenomena involved such as hydration, ionization and hydrolysis, also associated with energy changes which are usually positive and may more than counter-balance the first effect. But in general the heat of solution of hydrous neutral salts and of non-electrolytes is negative and of the order of some thousands of calories per gram equivalent.

In considering the theory of colloidal dispersion a knowledge of the energy changes involved is important. Many writers maintain that the phenomena of colloidal dispersion are identical with those of true solution save in the final size of the particles; that, in other words, true solution is merely the limiting case of colloidal dispersion. This being the case, colloids must have a "heat of peptization" of the same nature as the heat of crystalloidal solution. It is reasonable to assume that these heat effects arise from the work required to subdivide the solid and are at least roughly proportional to the specific surface developed by the dispersed phase. Taking the diameter of the molecules of a certain substance as  $0.1\mu\mu$  and the diameter of its colloiddally dispersed particles as  $10\mu\mu$ , the "heat of peptization" should then be about one hundredth part of the heat of solution, that is, of the order of some tens of calories per gram equivalent. On the other hand, if crystalloidal solution takes place by a process different from that of colloidal dispersion, we should not

<sup>1</sup> Abstract of a thesis submitted by F. L. Browne to the Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Quoted from Jones, "Nature of Solution," D. van Nostrand Co., 1917, p. 226.

<sup>3</sup> Graham, *il. Trans.*, 151, 220 (1861).

<sup>4</sup> Linder and Picton, *J. Chem. Soc.*, 61, 144, 146, 153 (1892).



expect to find any relation between heat of solution and "heat of peptization."

It is to be understood that by the term "heat of peptization" is meant merely the heat change involved in the subdivision of the solid phase and it is to be distinguished from the heat of wetting, heat of adsorption of substances in solution, or other heat effects due to the presence of substances in true solution. The converse of the "heat of peptization," *i. e.*, the energy change involved in the precipitation of the colloidal dispersion, will be called the "heat of coagulation."

Doerincel<sup>5</sup> has pointed out that the small amount of literature concerning the heat of coagulation of colloids is contradictory and inconclusive. He found that measurable amounts of heat are evolved on coagulating ferric oxide and silica hydrosols with electrolytes; his sols, however, contained large amounts of electrolytes and the magnitude of the heat effect on coagulation was greatly decreased on partly removing these by dialysis, although he did not seem to attach much significance to this fact. Kruyt and van der Spek<sup>6</sup> extended these experiments to the coagulation of arsenous sulfide hydrosol, finding that no measurable heat change accompanied the coagulation in this case. They concluded that the heat effects during the coagulation of ferric oxide sol are to be attributed to changes in the degree of hydration of the ferric oxide. For the case of arsenous sulfide they pointed out that no measurable amount of heat could be produced by interaction of the electrolytes in the sol and in the coagulant, but they completely ignored this possibility in the case of ferric oxide sol.

### Experimental Methods.

The determination of the heat changes accompanying the coagulation of colloids presents unusual difficulty because the magnitude of the heat effect per unit weight of dispersed phase is small, and the concentration of the colloid is usually low, consequently the temperature change to be measured is very small.

The apparatus employed was the familiar "submarine" type of the Richards adiabatic calorimeter.<sup>7</sup> The calorimeter vessel was a silver beaker of 700cc. capacity. This was placed in the "submarine" and the whole immersed in a bath of water constituting the "environment." The water of the environment was kept in rapid circulation by means of two powerful propeller stirrers, and its temperature could be very quickly altered by means of an electrical heating coil or by opening a valve admitting ice-water. A 4-junction copper-constantan thermo-element, connected to a sensitive galvanometer registering by means of a spot of light on a ground-glass scale, was placed with one limb in the liquid in the calorimeter vessel, the other in the environment, so that the difference in temperature between the two could be read at all times. Through-

<sup>5</sup> Doerincel, *Z. anorg. Chem.*, 66, 20 (1910); 67, 161 (1910).

<sup>6</sup> Kruyt and van der Spek, *Koll. Z.*, 24, 145 (1919).

<sup>7</sup> Richards and Rowe, *Proc. Am. Acad.*, 49, 173 (1913). Daniels, *THIS JOURNAL*, 38, 1473 (1916). MacInnes and Braham, *ibid.*, 39, 2110 (1917).

out an entire experiment this temperature difference was maintained within  $0.006^{\circ}$  of the desired value; after a sudden change in the temperature of the contents of the calorimeter amounting to  $1^{\circ}$  (very much larger than the temperature changes actually encountered) this temperature difference between environment and calorimeter contents could be restored to the desired value within 15 to 30 seconds.

The sample of the colloid to be coagulated was placed in the calorimeter vessel. Within this was suspended a silver cylinder closed at the bottom by a sheet of rubber dam held in place by a rubber band. The solution of the electrolyte used as coagulant was placed in this inner cylinder, or "mixing chamber." By means of mechanical stirrers, both the colloid and the coagulant were vigorously agitated. When the entire contents of the calorimeter had come to the same temperature, the temperature of the environment was so adjusted with respect to that of the calorimeter contents that the temperature of the latter remained constant. This was the case when the environment was very slightly cooler than the calorimeter contents, so that there was a loss of heat to the environment just equal to the heat generated by the operation of the mechanical stirrers. When this relation between environment and calorimeter temperatures had been found and the temperature of the calorimeter contents remained constant for a period of 10 minutes or more, the colloid and coagulant were mixed by operating a trigger which slipped off the rubber band holding the rubber bottom of the mixing chamber in place, and the entire silver cylinder was lowered slightly so as to be completely submerged in the mixed liquids in the calorimeter vessel. The same relation between the calorimeter and environment temperature was maintained until the calorimeter temperature again became constant, giving the end-point of the reaction.

The temperature of the calorimeter contents was measured by means of a Leeds and Northrup platinum resistance thermometer and thermometer bridge, the readings being estimated to  $0.0001^{\circ}$ . Instead of determining the water equivalent of the calorimeter and the specific heats of the liquids used, at the beginning of each experiment a measured quantity of electrical energy was converted into heat by means of a resistance coil submerged in the liquids in the calorimeter, and the resulting rise in temperature measured. This gave the amount of energy required to raise the calorimeter and contents  $1^{\circ}$ , and by multiplying this by the temperature change resulting upon mixing the liquids, the amount of heat liberated was obtained.

Under certain circumstances the method of operation was not as simple as described above. The stirring of the liquids in the calorimeter generated a certain amount of heat in consequence of which the temperature of the environment was maintained slightly below that of the liquids in the calorimeter in order that this amount of heat might be lost to the environment. If on coagulating the sol the resistance to the stirrers was greatly increased, heat was generated more rapidly than it was being lost to the environment, and at the end of the reaction the temperature did not remain constant, but rose slowly. In a number of the experiments in which the coagulum was especially gelatinous and bulky this proved to be the case. The difficulty was met by plotting the temperature-time curve for the 20 to 30 minutes following the mixing of the liquids. The temperature rose very rapidly for 1 or 2 minutes, then more slowly, and finally at a constant rate of the order of  $0.0002^{\circ}$  per minute. This constant rise in temperature was due to the added amount of heat generated as a result of the extra resistance to the stirrers. The straight line forming the last part of the temperature-time curve was extrapolated back to the time of mixing the liquids and the corresponding temperature taken as the end-point of the reaction.

The heat effect observed on mixing a sample of a sol with a solution of an electrolyte in this way included the heats of dilution of the sol with the

water in the electrolyte solution, and of the electrolyte solution with the water in the sol. In separate experiments, another sample of the sol was diluted with a volume of water equal to that of the coagulant, and another portion of the coagulant with a volume of water equal to that of the sol. These heats of dilution were then subtracted from the total heat effect on mixing sol and coagulant to give the "heat of coagulation."

Under the most favorable conditions the temperature difference was measured with an accuracy of  $0.0002^\circ$ , so that, allowing a similar amount for imperfect adiabaticity, the heat change was determined within about 0.25 gram calorie, corresponding to about 0.5 calorie per gram equivalent of ferric oxide for the more concentrated sols used. Where the coagula were very bulky and gelatinous, however, the errors were greater, so that the results cannot be relied upon closer than 1 or 2 calories per gram equivalent of ferric oxide.

#### Preparation of the Hydrosols.

Graham's method of mixing ferric chloride and ammonium carbonate solutions and dialyzing was used for the preparation of the ferric oxide hydrosols. 400 g. of ferric oxide was dissolved in a liter of water, filtered, and then 1000 cc. of a saturated solution of ammonium carbonate added slowly with constant stirring. Nine liters having been prepared in this way, it was dialyzed through collodion sacks. As soon as the purification had proceeded far enough to permit heating the sol to  $80^\circ$  without causing partial coagulation, the method of hot dialysis<sup>3</sup> was used. Experiment showed that the heat of coagulation of sols of the same purity prepared by hot dialysis and by cold dialysis is the same.

The sols were analyzed for ferric oxide and for chlorine. Following the nomenclature of Neidle, the ratio of gram equivalents of ferric oxide per liter to gram equivalents of chlorine per liter is called the "purity" of the sol.

#### Results.

**Heat of Dilution of Ferric Oxide Hydrosols.**—A 9-liter batch of colloid having been prepared, it was given a number for purposes of identification, and subjected to dialysis. As it attained different degrees of purity, samples were withdrawn, analyzed, and divided into portions for measurements of heats of coagulation and of dilution. Table I gives the data obtained on dilut-

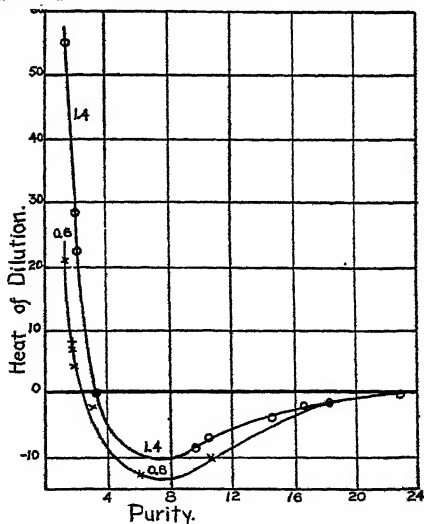


Fig. 1.—The heat of dilution per g. equiv. of  $\text{Fe}_2\text{O}_3$  as a function of the purity of the sol for ferric oxide hydrosols containing, respectively, 1.4 and 0.6 g. equiv. of  $\text{Fe}_2\text{O}_3$  per liter. The marked heat effects with the less pure sols disappear when the purity exceeds 22.

<sup>3</sup> Neidle and Barab, *THIS JOURNAL*, 39, 71 (1917).

ing 340cc. portions of such sols with 240 cc. of water. The first column gives the number of the sol, the second the purity, the third the content of ferric oxide and of chlorine, the fourth the observed

TABLE I.  
HEAT OF DILUTION OF FERRIC OXIDE SOL.  
340 cc. of sol diluted with 240 cc. of water.

Sol. No.	Purity.	Concentration g. equiv. per liter.		Heat effect calories.	Heat of dilution per g. equiv.	
		Fe <sub>2</sub> O <sub>3</sub> .	Cl.		Fe <sub>2</sub> O <sub>3</sub> .	Cl.
8	1.490	1.500	1.007	+29.2	+57.3	+85.4
		0.750	0.504	+ 7.6	+29.7	+44.2
		0.375	0.252	0.0	0.0	0.0
6	1.840	1.443	0.784	+ 4.0	+ 8.1	+15.0
		0.846	0.460	+ 2.1	+ 7.3	+13.4
		0.496	0.270	+ 1.2	+ 7.1	+13.1
8	2.054	1.198	0.583	+ 9.3	+22.8	+46.9
		0.599	0.292	+ 0.9	+ 4.4	+ 9.1
14	2.093	1.446	0.691	+11.8	+23.9	+50.1
6	3.362	1.440	0.428	0.0	0.0	0.0
		0.844	0.251	- 0.6	- 2.1	- 7.0
		0.495	0.147	- 0.3	- 1.8	- 6.0
8	3.373	1.242	0.368	+ 0.3	+ 0.7	+ 2.4
8	6.127	1.455	0.237	- 4.7	- 9.6	-58.7
		0.728	0.119	- 3.2	-12.9	-78.7
6	9.750	1.653	0.169	- 4.3	- 7.7	-74.9
7	10.59	1.578	0.149	- 3.5	- 6.6	-69.8
		0.789	0.075	- 2.5	- 9.4	-99.4
		0.395	0.037	- 1.3	- 9.4	-99.3
7	14.66	1.547	0.106	- 1.4	- 2.7	-40.1
6	16.67	1.428	0.086	- 0.6	- 1.2	-20.6
7	18.30	1.44	0.079	- 0.6	- 1.2	-22.4
7	22.97	1.41	0.063	0.0	0.0	0.0
6	31.88	1.52	0.048	0.0	0.0	0.0

heat effect, and the fifth the heat effect in calories per gram equivalent of ferric oxide and in calories per gram equivalent of chlorine in the sol. For each purity, a curve was drawn showing the heat of dilution per gram equivalent of ferric oxide as a function of the concentration of the sol. By selecting a line of constant concentration and reading its intersections with the curves for the different purities, the data were obtained for Fig. 1, which gives the heat of dilution per gram equivalent of ferric oxide as a function of the purity. Fig. 2 is drawn on the assumption that the heat effects are due entirely to the electrolytes in the sol. Taking the chlorine content as the measure of these electrolytes, the heat of dilution per gram equivalent of chlorine is plotted against the concentration of chlorine in the sol. In this figure is shown also the heat of dilution of ferric chloride solutions of varying concentration, the data for which are given in Table II.

TABLE II.  
HEAT OF DILUTION OF FERRIC CHLORIDE.  
360 cc. of ferric chloride solution diluted with 255 cc. of water.

Concentration $\text{FeCl}_3$ g. equiv. per liter.	Heat effect calories.	Heat of dilution per g. equiv. $\text{FeCl}_3$ .
1.029	+70.5	+190.3
0.515	+18.7	+100.8
0.257	+ 2.9	+ 31
0.129	- 1.8	- 38
0.064	- 2.7	-116
0.032	- 2.2	-191
0.016	- 1.1	-192
0.008	- 0.3	- 90

Heat of dilution of a solution containing 0.0643 g. equiv. of  $\text{FeCl}_3$  and 0.0625 g. equiv. of  $\text{NH}_4\text{Cl}$  per liter was -1.95 calorie.

The freshly prepared hydrosols have a positive heat of dilution which rapidly decreases in magnitude as the dialysis proceeds, soon reaching zero and then becoming negative, passing through a minimum at a purity between 7 and 8, finally rising to zero beyond a purity of 21 or 22. Fig. 2 shows that ferric chloride solutions behave similarly on dilution. This suggests that the heat effect observed on dilution of the colloid may be due to the presence of ferric chloride. An observation by Neidle<sup>8</sup> lends support to this view. He noted that when a sol with a purity less than 21 is coagulated with sodium sulfate, for example, and the supernatant liquid tested for ferric ion by means of thiocyanate, a positive test results, but with sols having a purity greater than 21 the test is negative.

The curves in Fig. 2 confirm this assumption. If all the chlorine in the sol represented ferric chloride and the dilution of this salt were the only cause of a heat

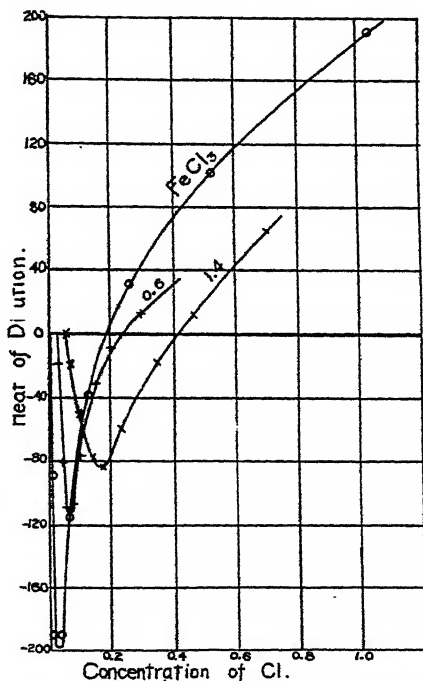
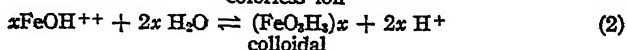
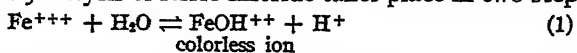


Fig. 2.—The heat of dilution per g. equiv. of Cl in the sol plotted against the concentration of Cl in the sol for ferric oxide sols containing, respectively, 1.4 and 0.6 g. equiv. of  $\text{Fe}_2\text{O}_3$  per liter, together with the heat of dilution of ferric chloride solutions of varying concentration. The similarity in the shapes of these curves suggests that the heat effects on diluting ferric oxide sols are due to the ferric chloride contained in them.

effect, the curves for the colloids and for the dilution of ferric chloride would coincide. But the first of these assumptions is known to be incorrect, for part of the chlorine represents ammonium chloride, a by-product of the reaction by which the sol was prepared, and a part probably represents hydrochloric acid. In addition the presence of the colloidal ferric oxide undoubtedly results in the adsorption of a part of the electrolytes present. The present state of our knowledge of ferric oxide sol does not permit us to make corrections for these factors quantitatively, but considering them qualitatively we see that, since the heat of dilution of ammonium chloride or of hydrochloric acid in the concentrations present is negligible, the curves for the colloids tend to coincide with that for the ferric chloride solutions. The close similarity in the shapes of the curves together with the fact that after the sols have reached a purity of 21 the heat of dilution is zero, show definitely that the observed heat effects are to be attributed to the electrolytes present in the sol.

When a ferric chloride solution is diluted in the calorimeter there results first a rapid evolution or absorption of heat, depending upon the concentration of the solution used, followed by a slow rise in temperature of the order of magnitude of  $0.001^\circ$  per minute. This secondary evolution of heat continues for hours, but during the first 15 or 20 minutes at least it takes place at a constant rate. For present purposes we are interested only in the first large heat change. The temperature of the calorimeter contents was therefore taken at intervals and plotted against the time. The curve became a straight line within a few minutes after the dilution took place, and was extrapolated back to the time of mixing to give the final temperature of the contents of the calorimeter.

Goodwin<sup>9</sup> observed a similar phenomenon in his study of the conductivity of ferric chloride solutions. When a ferric chloride solution is quickly diluted and the conductivity measured at intervals, this is found to increase slowly for a number of hours. Moreover, the diluted solutions which are at first nearly colorless gradually take on the red color characteristic of colloidal ferric oxide. Goodwin explained the phenomenon on the basis of the theory that the hydrolysis of ferric chloride takes place in two steps.



The first step is an instantaneous reaction, but the second requires time. The second step resembles a supersaturation phenomenon in that it proceeds more readily if the solution is first "seeded" with ferric oxide sol, the particles of which are assumed to act as nuclei for the further condensation of ferric oxide.

These experiments on the heat of dilution of ferric chloride solutions

<sup>9</sup> Goodwin, *Phys. Rev.*, 9, 251 (1896); 11, 193 (1900).

indicate that Reaction 1 is strongly endothermal and Reaction 2 exothermal. It should be noted, however, that the thermal data confirm the conclusion that the hydrolysis takes place in two steps, the first a rapid and the second a slow reaction, but do not add any conclusive evidence regarding the nature of the hypothetical intermediate product which Goodwin assumed

TABLE III.

HEAT OF MIXING OF FERRIC CHLORIDE WITH ELECTROLYTES.

360 cc. of  $\text{FeCl}_3$  solution mixed with 255 cc. of electrolyte.(For heat of dilution of  $\text{FeCl}_3$  see Table II.)Heat of dilution of 255 cc. of electrolytes with 360 cc. of  $\text{H}_2\text{O}$ .

0.1 N $\text{Na}_2\text{C}_2\text{O}_4$	+ 0.6 cal.	0.1 N $\text{K}_3\text{Fe}(\text{CN})_6$	0.00
0.221 N $\text{Na}_2\text{SO}_4$	- 1.32	0.196 N $\text{H}_2\text{SO}_4$	+15.2
0.5 N $\text{NaCl}$	- 4.40		

Electrolyte.	Concentration $\text{FeCl}_3$ .	Heat effect calories.	Heat of mixing.	Heat of mixing per g. equiv. of $\text{Cl}$ .
0.1 N $\text{Na}_2\text{C}_2\text{O}_4$	1.029	+ 69.6	- 1.6	- 4.3
	0.515	16.4	- 3.0	- 15.9
	0.257	0.0	- 3.5	- 37.4
	0.129	0.0	+ 1.2	+ 25.1
	0.064	4.6	+ 6.7	+ 239
	0.032	7.6	+ 9.2	+ 794
	0.016	4.6	+ 5.1	+ 886
	0.008	4.4	+ 4.0	+1385
0.221 N $\text{Na}_2\text{SO}_4$	1.029	- 61.2	-130.4	- 352
	0.515	-116.9	-133.0	- 717
	0.257	-123.0	-129.5	-1400
	0.129	- 93.3	- 90.2	-1940
	0.064	- 54.8	- 50.8	-2200
	0.032	- 26.8	- 23.3	-2030
	0.016	- 14.6	- 12.2	-2110
	0.008	- 7.4	- 5.8	-2030
0.5 N $\text{NaCl}$	1.029	+ 10.7	- 55.4	- 150
	0.515	- 22.4	- 36.7	- 198
	0.257	- 23.8	- 22.2	- 240
	0.129	- 18.4	- 12.3	- 264
	0.064	- 13.6	- 6.5	- 283
	0.032	- 9.0	- 2.4	- 208
	0.016	- 7.3	- 1.8	- 307
	0.008	- 7.3	- 1.8	- 307
0.1 N $\text{K}_3\text{Fe}(\text{CN})_6$	1.029	+ 73.2	+ 2.7	+ 7.3
	0.515	+ 14.6	- 4.1	- 22.2
	0.257	- 4.2	- 7.1	- 76.7
	0.129	- 9.2	- 7.4	- 160
	0.064	- 6.6	- 3.9	- 169
	0.032	- 2.9	- 0.7	- 63
0.196 N $\text{H}_2\text{SO}_4$	1.029	+118.8	+ 33.1	+ 89
	0.515	54.5	20.6	111
	0.257	27.6	9.5	103
	0.129	19.1	5.7	122
	0.064	18.5	5.9	253
	0.032	18.6	5.6	487

to be  $\text{FeOH}^+$ . From the high heat of formation of water from its ions and the exothermal character of Reaction 2 we should prefer to write it in such a way as to involve the decomposition of fewer molecules of water.

**Heat of Mixing of Ferric Chloride with Electrolytes.**—The stock ferric chloride solution was 1.029 *N* and the ratio of equivalents of iron to equivalents of chlorine was 1.000. From this a series of dilutions was prepared, and the heat effect determined on mixing 360 cc. with 255 cc. of the electrolyte solution used for the coagulation of the ferric oxide sols.

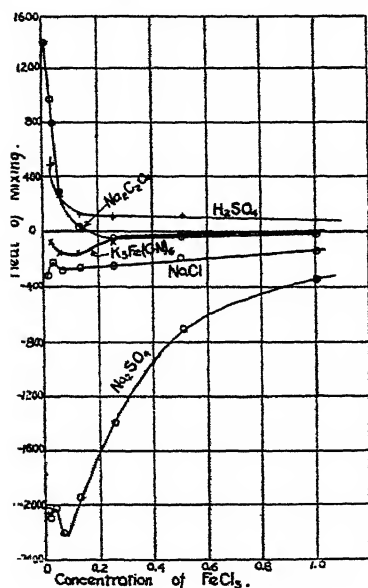


Fig. 3.—The heat of mixing of solutions of electrolytes with solutions of ferric chloride of varying concentration.

The electrolytes used were sodium oxalate, sodium sulfate, sodium chloride, potassium ferricyanide, sulfuric acid, and sodium hydroxide. With each of these coagulants, the influence of the following factors on the heat of coagulation was determined: (1) the concentration of the hydrosol; (2) the purity of the sol; (3) the concentration of the coagulant.

A large batch of colloid having been prepared and subjected to dialysis, samples were withdrawn at various purities. With each sample a series of dilutions was prepared and observation made of the heat effect accompanying the coagulation with the electrolyte solution being studied. From the total heat effect observed were subtracted the heats of dilution of the sol and of the coagulant to obtain the heat of coagulation. Plotting the results gave a family of curves for sols of the different purities showing

From this were subtracted the heats of dilution of 360 cc. of the ferric chloride with 255 cc. of water, and of 255 cc. of the electrolyte solution with 360 cc. of water, the difference being the heat of mixing of the ferric chloride and the electrolyte solution. The data are given in Table III and Fig. 3.

The very significant values for the heats of mixing are undoubtedly to be explained by the influence of the electrolytes upon Reaction 1 in the hydrolysis of the ferric chloride. Moreover, in the coagulation of ferric oxide sols having a purity less than about 22 this heat of mixing of the electrolyte with the ferric chloride present in the sol will be expected to play an important part.

**Heat of Coagulation of Sols with Electrolytes.**—Since ferric oxide hydrosol is positively charged, the anions are the effective ions in coagulation.



the heat of coagulation as a function of the concentration of the sol. Selecting lines of constant concentration and reading their intersections with the curves for the different purities gave the data from which curves showing the heat of coagulation as a function of the purity, the concen-

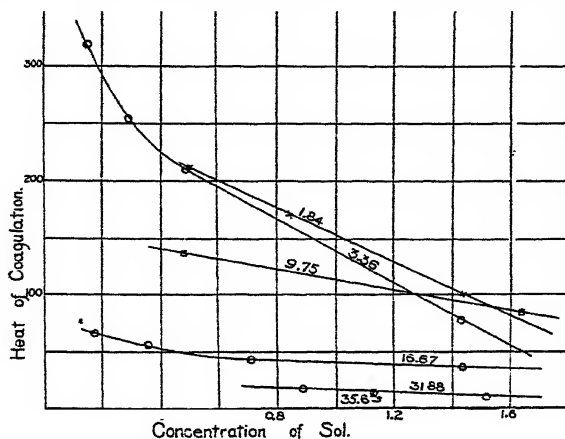


Fig. 4.—The heat of coagulation of ferric oxide sols of varying concentration with 0.1  $N$   $\text{Na}_2\text{C}_2\text{O}_4$ . The numbers on the curves give the purity of the sol.

TABLE IV.

HEAT OF COAGULATION OF FERRIC OXIDE SOL OF VARYING CONCENTRATION AND PURITY WITH 0.1  $N$  SODIUM OXALATE.

340 cc. of sol No. 6 mixed with 240 cc. of 0.1 $N$ $\text{Na}_2\text{C}_2\text{O}_4$ .						
(Heat of dilution of 240 cc. $\text{Na}_2\text{C}_2\text{O}_4$ with 340 cc. $\text{H}_2\text{O}$ , + 0.6 cal.)						
Purity.	Concentration g. equiv. per liter. $\text{Fe}_2\text{O}_3$ . Cl.		Heat effect calories.	Ht. of dil'n of sol.	Heat of coag'l'n per g. equiv. $\text{Fe}_2\text{O}_3$ . Cl.	
1.84	1.443	0.784	+55.1	+4.0	+103	+189
	0.846	0.495	52.0	+2.1	171	315
	0.496	0.269	27.8	+1.2	214	395
3.362	1.440	0.429	40.5	0.0	81	274
	0.844	0.251	47.1	-0.6	164	552
	0.495	0.147	35.8	-0.3	211	708
	0.290	0.086	25.5	-0.2	254	853
	0.145	0.043	16.3	-0.1	320	1074
9.75	0.073	0.022	14.1	-0.1	550	1850
	1.653	0.170	45.4	-4.3	87	852
16.67	0.485	0.050	21.9	-1.3	137	1340
	1.428	0.086	18.0	-0.6	37	618
31.88	0.714	0.043	11.1	-0.3	45	746
	0.357	0.021	7.6	-0.2	59	979
	0.179	0.011	4.6	-0.1	67	1220
35.6	1.519	0.048	7.1	0.0	13	403
	0.891	0.028	5.9	0.0	19	619
	1.14	0.032	6.9	0.0	16	578

tration of the sol remaining constant, were obtained. Finally, using a sample of colloid having constant purity and concentration, the heat of coagulation with solutions of the electrolyte in varying concentration was measured, correction being made as usual for the heats of dilution of the sol and of the electrolyte. The concentration of the coagulants was varied over wide limits, the most dilute solution lying well below the limiting concentration so that the sols were not coagulated by them.

Tables IV to VI give the data for the heat of coagulation of sols of different purity and concentration with the six different electrolytes. The first column gives the purity of the sol, the second the concentration of ferric oxide and of chlorine in the sol, the third the observed heat effect, the fourth the heat of dilution of the sol and of the coagulant, and the fifth the heat

TABLE V.

HEAT OF COAGULATION OF FERRIC OXIDE SOL OF VARYING CONCENTRATION AND PURITY WITH SODIUM SULFATE.

340 cc. of sol No. 6 or 7 mixed with 240 cc. of  $\text{Na}_2\text{SO}_4$ .  
(Heat of dil'n 0.313 N  $\text{Na}_2\text{SO}_4$  -2.3 cal.; 0.157 N, 0.0 cal.)

Purity.	Concentration g. equiv. per liter.			Heat effect calories.	Ht. of dil'n of sol.	Ht. of coag'n per g. equiv.	
	$\text{Fe}_2\text{O}_3$ .	Cl.	$\text{Na}_2\text{SO}_4$ .			$\text{Fe}_2\text{O}_3$ .	Cl.
1.490	1.500	1.008	0.313	-557.9	+29.2	-1147	-1708
	0.750	0.503	0.157	-36.9	+7.6	-175	-260
	0.375	0.252	0.078	-22.5	+0.0	-177	-263
2.054	1.198	0.584	0.313	-85.4	+9.3	-227	-460
	0.599	0.292	0.157	-45.5	+0.9	-228	-468
3.373	1.242	0.369	0.313	-74.0	+0.3	-171	-575
	0.621	0.184	0.157	-37.9		-179	-604
6.127	1.455	0.238	0.313	-26.0	-4.7	-38	-235
	0.728	0.119	0.157	-7.9	-3.2	+19	+118
8.26	1.537	0.186	0.313	+17.3	-5.0	+47	+389
	0.768	0.093	0.157	+12.4	-3.6	+62	+515
10.59	1.578	0.149	0.313	+21.1	-3.5	+50	+531
	0.789	0.075	0.157	+14.2	-2.5	+62	+658
	0.395	0.137	0.078	+9.0	-1.3	+67	+712
	0.197	0.018	0.039	+5.3	-0.6	+88	+934
	0.098	0.009	0.020	+3.6	-0.3	+117	+1237
11.76	1.401	0.119	0.313	+19.3	-2.8	+51	+602
	0.701	0.060	0.157	+14.4	-1.6	+67	+986
14.66	1.547	0.105	0.313	+15.8	-1.4	+37	+543
	0.774	0.053	0.157	+10.3	-0.7	+42	+614
	0.387	0.026	0.078	+7.2	-0.4	+57	+842
	0.193	0.013	0.039	+4.0	-0.2	+63	+921
14.77	1.326	0.090	0.313	+14.0	-1.5	+39	+580
18.30	1.44	0.079	0.313	+7.0	-0.6	+20	+370
	0.72	0.040	0.157	+4.6	-0.3	+20	+368
	0.36	0.020	0.078	+2.9	-0.2	+25	+452
22.97	1.44	0.063	0.313	+5.3	0.0	+15	+354
28.02	1.44	0.051	0.313	+5.4	0.0	+16	+441
39.29	0.77	0.019	0.100	+3.6	0.0	+13	+516

TABLE VI.

HEAT OF COAGULATION OF FERRIC OXIDE SOL OF VARYING CONCENTRATION AND PURITY WITH SODIUM CHLORIDE, POTASSIUM FERRICYANIDE, SULFURIC ACID AND SODIUM HYDROXIDE.

360 cc. of sol with 255 cc. of coagulant.

Coagulant.	Purity.	Concentration g. equiv. per liter.		Heat effect calories.	Ht. of dil'n sol. coagulant.		Hg. of coag't'n per g. equiv.	
		FeO <sub>3</sub> .	Cl.				FeO <sub>3</sub> .	Cl.
0.5 N NaCl	2.093	1.446	0.691	- 11.5 <sup>a</sup>	+11.8	- 4.4	- 36	- 76
		0.723	0.346	- 17.6 <sup>a</sup>	+ 1.2		- 55	- 116
		0.362	0.173	- 13.3 <sup>a</sup>	+ 0.1		- 69	- 144
	6.037	1.153	0.191	- 14.3 <sup>a</sup>	- 4.2		- 14	- 83
		0.577	0.096	- 9.2 <sup>a</sup>	- 2.8		- 9	- 57
		0.288	0.048	- 6.4 <sup>a</sup>	- 1.9		- 0.6	- 3
	9.802	1.540	0.157	- 4.2 <sup>a</sup>	- 3.6		+ 7	+ 70
		0.770	0.079	- 2.2 <sup>a</sup>	- 1.1		+ 12	+ 117
	15.55	1.305	0.084	- 3.3	- 1.0		+ 5	+ 71
		0.653	0.042	- 3.7	- 0.3		+ 4	+ 64
	22.96	1.095	0.048	- 3.6	0.0		+ 2	+ 49
0.1 N K <sub>3</sub> Fe(CN) <sub>6</sub>	2.093	1.446	0.691	+ 31.5	+11.8	0.0	+ 38	+ 79
		0.723	0.346	7.3	+ 0.1		55	116
		1.153	0.191	4.5	- 4.2		21	126
	6.037	0.567	0.096	2.7	- 2.8		27	161
		0.288	0.048	1.5	- 1.9		33	197
		1.540	0.157	12.2	- 3.8		29	231
	9.802	0.770	0.079	8.3	- 1.1		34	331
		0.385	0.039	4.6	- 0.4		36	350
	14.72	1.305	0.089	6.0	- 1.4		16	230
	15.55	1.305	0.089				15	228
		0.653	0.042	2.6	- 0.3		12	183
	22.96	1.095	0.048	0.7	0.0		1.8	42
0.199 N NaOH	2.093	1.446	0.691	+462.0 <sup>a</sup>	+11.8	- 1.0	+ 870	+1820
		0.723	0.346	430.5 <sup>a</sup>	+ 1.2		1653	3460
		0.362	0.173	330.7	+ 0.1		2548	5335
	6.037	1.153	0.191	341.5	- 4.2		835	5045
		0.577	0.096	190.0	- 2.8		934	5662
		0.288	0.048	111.5	- 1.9		1103	6660
	9.802	1.540	0.157	230.5	- 3.8		424	4160
		0.770	0.079	151.8	- 1.1		555	5445
	15.55	0.390	0.039	83.0	- 0.4		609	5965
		0.653	0.042	52.4	- 0.3		229	3556
	22.96	0.326	0.021	35.5	0.0		311	4230
		1.095	0.048	47.3	0.0		123	2830
0.196 N H <sub>2</sub> SO <sub>4</sub>	2.093	0.548	0.024	28.5	0.0		149	3430
		1.446		+103	+11.8	+15.2	+ 146	
		0.723		68	+ 1.2		200	
	6.037	0.367		39	+ 0.1		181	
		1.153	0.191	103	- 4.2		221	1330
		0.577	0.096	58	- 2.8		220	1325
	9.802	0.139	0.048	26	- 1.3		240	1445
		1.540	0.157	127	- 4.8		209	2045
		0.770	0.078	77	- 1.1		225	2210

TABLE VI (continued).

Coagulant.	Purity.	Concentration g. equiv. per liter. $\text{Fe}_2\text{O}_3$	Concentration Cl.	Heat effect calories.	Ht. of dil'n sol. coagulant.	Ht. of coag'l'n per g. equiv. $\text{Fe}_2\text{O}_3$	Ht. of coag'l'n per g. equiv. Cl.
		0.385	0.039	+47	-0.4	+234	+2297
	15.55	0.635	0.042	73	-0.3	249	3870
		0.326	0.021	47	0.0	268	4162
	22.96	1.095	0.048	129	0.0	287	6600
		0.548	0.024	72	0.0	287	6580

<sup>a</sup> The sols did not coagulate in these experiments.

of coagulation per gram equivalent of ferric oxide and per gram equivalent of chlorine in the sol. Fig. 4 shows the heat of coagulation per gram equivalent of ferric oxide as a function of the concentration of the sol in the case of 0.1 *N* sodium oxalate as coagulant. The corresponding curves for the other electrolytes are similar in character. In Fig. 5 the

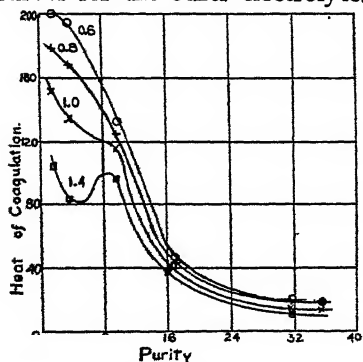


Fig. 5.—The heat of coagulation with 0.1 *N*  $\text{Na}_2\text{C}_2\text{O}_4$  of ferric oxide sols containing, respectively, 0.6, 0.8, 1.0 and 1.4 g. equiv. of  $\text{Fe}_2\text{O}_3$  per liter, as a function of the purity of the sol. At the higher purities the heat effects become very small.

heat of coagulation per gram equivalent of ferric oxide is plotted against the purity for sols containing 0.6, 0.8, 1.0, and 1.4 gram equivalents of ferric oxide per liter, the coagulant being 0.1 *N* sodium oxalate. Fig. 6 gives the heat of coagulation per gram equivalent of ferric oxide as a function of the purity for all six electrolytes used, the concentration of the sol being 1.0 gram equivalent of ferric oxide per liter.

These curves show in a striking manner that the heat effects are large only when the sol contains large amounts of electrolytes. As these are removed by dialysis, the heat effect falls off very rapidly, eventually falling within the experimental error at a purity of about 23

in the cases of sodium chloride and potassium ferricyanide as coagulants. With sodium sulfate and potassium oxalate at this purity the heat of coagulation is small, but still measurable. The curves could not be carried much farther in the direction of greater purity, however, because of the experimental difficulty of preparing such concentrated sols of high purity, and also because the coagulum formed from sols of such high purity becomes so bulky and gelatinous that the contents of the calorimeter can no longer be adequately stirred, and the generation of heat by friction with the stirrers becomes large enough to introduce serious error.

Clearly the observed heat effects are due to the presence of the electrolytes in the sol and not to the change in the dispersity of the ferric oxide during coagulation. This is shown not only by the fact that the heat

effect disappears when the electrolytes are removed from the sol, but by the great variation in the shape of the curves for the different electrolytes in the region of low purity. With sodium sulfate and sodium chloride the curves have negative as well as positive branches. It seems probable that the heat effects may be attributed entirely to the shift in the equilibrium of Reaction 1 in the hydrolysis of ferric chloride. As has already been pointed out, in our present state of knowledge of ferric oxide sol we do not know very much about the constitution of the sols and the concentrations of the electrolytes present, consequently it is not yet possible to test this theory quantitatively.

Sulfuric acid as coagulant behaves very differently from the other electrolytes in that the heat of coagulation increases with increasing purity. In these experiments, on mixing the sol with the coagulant in the calorimeter, a sudden change in temperature resulted, followed by a slow rise in temperature at a rate of the order of  $0.004^\circ$  per minute continuing indefinitely. The first rapid change in temperature was measured in these experiments. These phenomena are easily understood if we consider that the solution of ferric oxide (sol or gel) in dilute acids takes place through a reversal

of the two reactions by which ferric chloride hydrolyzes. In all cases, then, we have the dispersed phase in equilibrium with the intermediate product according to Equation 2, and the latter in equilibrium with ferric ion according to Equation 1. Addition of sulfuric acid by increasing the hydrogen-ion concentration forces the equilibrium of Reaction 1 to the left, decreasing the concentration of the intermediate product, and this in turn causes more of the ferric oxide to pass into solution according to Equation 2.

In Fig. 7 is shown the heat of coagulation of ferric oxide sols of constant purity and concentration with solutions of the six electrolytes of varying

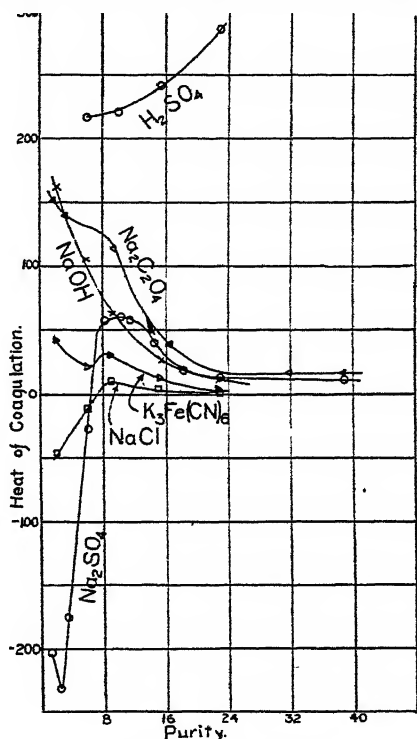


Fig. 6.—The heat of coagulation of ferric oxide sols containing 1.0 g. equiv. of  $\text{Fe}_2\text{O}_3$  per liter with different electrolytes as a function of the purity of the sol.

concentration. The data for these curves are given in Table VII. In every case the heat effect increases rapidly at first as the concentration of the coagulant increases, but soon reaches a point beyond which the change is very small. The limiting concentration of the electrolyte in

TABLE VII.

HEAT OF COAGULATION OF FERRIC OXIDE SOL. WITH COAGULANTS OF VARYING CONCENTRATION.

360 cc. of sol with 255 cc. of coagulant.							
Coagulant.	Concn. of coagulant g. equiv. per liter.	Purity of sol.	Concn. of sol g. eq. per liter.	Heat effect calories.	Ht. of dil'n sol.	Ht. of dil'n coagulant.	Ht. of coag'n per g. equiv. $\text{Fe}_2\text{O}_3$ .
$\text{Na}_2\text{C}_2\text{O}_4$	0.250	11.76	1.337	+ 37.4	-3.0	+ 1.4	+ 81.1
	0.050			22.4		0.0	52.9
	0.040			18.9*		0.0	45.6
	0.025			14.3*		0.0	36.0
	0.250	15.85	1.305	+ 13.2	-1.0	+ 1.4	+ 27.3
	0.125			13.3		+ 0.6	29.2
	0.063			11.4		0.0	26.5
	0.031			8.7		0.0	20.5
	0.016			7.0*		0.0	17.0
	0.008			5.0*		0.0	13.0
$\text{Na}_2\text{SO}_4$	1.966	10.97	1.386	-135.4	-3.3	-159.2	+ 57.5
	1.474			- 37.2		- 56.0	47.3
	0.983			- 17.7		- 25.5	23.5
	0.492			+ 11.3		- 5.7	43.8
	0.246			+ 21.0		- 1.6	54.9
	0.123			+ 24.8		- 0.5	60.6
	0.098			+ 27.4		- 0.3	65.7
	0.080			+ 25.6*		0.0	63.3
	0.061			+ 24.6*		0.0	53.9
	0.031			+ 8.0*		0.0	24.0
	0.256	15.48	1.335	+ 14.7	-1.5	- 1.2	+ 36.1
	0.128			16.1		- 0.4	37.5
	0.064			18.9		0.0	42.4
	0.048			17.4		0.0	39.4
	0.032			16.5*		0.0	37.5
$\text{NaCl}$	0.500	15.55	1.305	- 3.3	-1.0	- 4.4	+ 4.6
	0.210			+ 4.1		0.0	10.9
$\text{K}_2\text{Fe}(\text{CN})_6$	0.500	14.72	1.305	- 3.8	-1.4	-10.4	+ 17.0
	0.100			+ 6.0		0.0	15.7
	0.025			+ 3.8*		0.0	11.1
$\text{NaOH}$	0.511	14.72	1.305	+112.1	-1.4	- 2.6	+247
	0.256			110.2		- 1.2	240
	0.102			97.4		- 0.5	211
	0.051			72.2		0.0	157
$\text{H}_2\text{SO}_4$	0.505	15.85	1.305	+138.6	-1.0	+ 26.7	+240
	0.252			126.2		17.6	233
	0.105			113.0		8.8	224
	0.073			92.9		2.1	196
	0.052			76.3*		1.6	161

\* The sols did not coagulate in these experiments.

each lies between the points marked A and B. It will be seen, therefore, that the curves do not attain their maximum until some time after the limiting concentration has been passed, and that there is no "break" in any of the curves at this point. This confirms the conclusion that the heat effects observed are due entirely to the electrolytes in the sol and

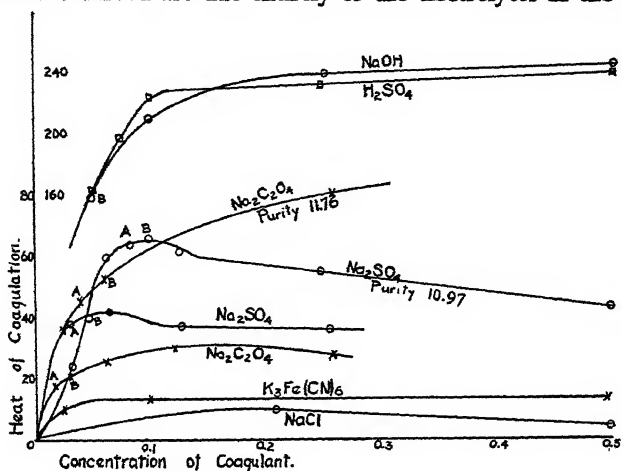


Fig. 7.—The heat of coagulation of ferric oxide sol with different electrolytes as a function of the concentration of the coagulant. The sol contained 1.3 g. equiv. of ferric oxide per liter and had a purity of 15 except where otherwise indicated. The limiting concentration of the electrolyte lies between the points marked A and B.

in the coagulant, and that the act of changing the dispersity of the ferric oxide during coagulation is not associated with any measurable heat change.

### Summary.

1. The dilution of ferric oxide hydrosols of varying purity is accompanied by measurable heat effects until the purity exceeds 21 or 22, beyond which point the heat of dilution is zero. If the heat of dilution per gram equivalent of chlorine in the sol is plotted against the chlorine content, the curve is of the same nature as that for the heat of dilution of ferric chloride solutions of varying concentration.

2. The thermal behavior of ferric chloride solutions on dilution confirms the observations of Goodwin based on conductivity to the effect that the hydrolysis of ferric chloride takes place in two steps, the first an instantaneous and the second a slow reaction.

3. The mixing of ferric chloride solutions with common electrolytes involves very significant heat changes.

4. The heats of coagulation of ferric oxide sols of varying purity with sodium oxalate, sodium sulfate, sodium chloride, potassium ferricyanide,

sodium hydroxide, and sulfuric acid have been determined. The curves showing the heat of coagulation as a function of the purity vary widely in shape with the nature of the coagulant, the heat effect being usually positive, but with sodium sulfate and sodium chloride at low purities, negative. As the purity increases the heat of coagulation becomes smaller, finally becoming negligible, except in the case of sulfuric acid. The peculiar behavior of the last electrolyte is due to solution of the ferric oxide.

5. When the heat of coagulation is plotted against the concentration of the coagulating electrolyte, smooth curves are obtained showing no "break" at the point of limiting concentration.

6. The heat effects observed on coagulating ferric oxide sols with electrolytes are to be attributed to the action of the electrolytes in the coagulants upon the electrolytes, particularly ferric chloride, present in the sol. The change in dispersity of the ferric oxide on coagulation does not involve a heat change greater than 1 to 2 calories per gram equivalent of ferric oxide.

7. In the case of ferric oxide hydrosol there exists no "heat of peptization" analogous to the heat of solution of crystalloids.

The work described in this paper has been carried out with the assistance of a fellowship established by E. I. duPont de Nemours and Company, to whom the authors wish to express their indebtedness.

MADISON, WISCONSIN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

## THE STRENGTHS OF COBALTAMMINE BASES AND WERNER'S THEORY OF BASES.

BY ARTHUR B. LAMB AND VICTOR YNGVE.

Received July 20, 1921.

The great strength of many cobaltamine bases has attracted the attention and evoked the surprise of investigators in this field. Cobaltic hexamine hydroxide (luteo cobaltic hydroxide), for instance, is a very soluble, deliquescent substance whose solution is caustic in its properties, absorbs carbon dioxide with avidity, and displaces both ammonia and silver oxide from their salts. Werner,<sup>1</sup> estimating the strengths of various ammine bases qualitatively from their chemical behavior and from the properties of their salts, has arranged certain of them in the order of their strengths, and indeed largely on the basis of these considerations has proposed a new theory of bases and of hydrolysis. We have therefore been interested to obtain quantitative measurements of the strengths of these bases. We have used the conductivity method for this purpose, measuring the conductivities of their dilute solutions at various concentrations and comparing the resulting molecular conductivities with the conductiv-

<sup>1</sup> Werner, "Neuere Anschauungen," 3rd edition, Braunschweig, 1913, p. 265.



ities at infinite dilution, as computed from measurements of the conductivities of salts derived from them.

Solutions of the bases were prepared by triturating their bromides with an excess of moist silver oxide, the mortar, pestle, silver oxide and water having all been carefully cooled to zero degrees. The solution was then rapidly filtered by suction into a graduated 250cc. flask, the residue washed several times with 10cc. portions of ice-cold water, and the solution made up to the mark. After thorough mixing, a portion was transferred to conductivity cells and the conductivity measured, first in an ice-bath and then in a 25° thermostat. Aliquot portions of the original solution were diluted successively and lower concentrations were then measured in the same way. The more important details of manipulation were as follows.

**Preparation of Materials.**—The water was prepared by redistillation using a little barium hydroxide and potassium permanganate. It and the solutions made from it were kept in carefully closed and steam-extracted resistance-glass bottles. Its conductivity was always measured before use.

Most of the amines were prepared according to the improved methods of Jørgensen.<sup>2</sup> The hexamine bromide was, however, made by precipitation with pure conc. hydrobromic acid of hexamine chloride prepared according to the method of Lamb and Larson.<sup>3</sup> It was then washed several times with dil. hydrobromic acid and with alcohol until all the acid was removed, and finally was dried in an air-bath at 35°. The triethylenediamine bromide was prepared from the hexamine bromide according to the method of Pfeiffer,<sup>4</sup> while the dibromo-diethylenediamine bromide, which on treatment with moist silver oxide gave diaquo-diethylenediamine cobaltic hydroxide was a commercial product.

The silver oxide was prepared by the action of a clear solution of barium hydroxide on an excess of silver nitrate in dilute solution. It was washed with a large amount of conductivity water until no test for barium ion could be obtained. It was kept under conductivity water in a closed vessel.

**The Apparatus.**—Three of the conductivity cells were flask-shaped vessels of Jena glass, provided with large strongly anchored sealed-in electrodes; one consisted of dip electrodes fitted into a wide-mouthed flask. Each was closed by a rubber stopper and was provided with a thermometer legible to 0.01°. A large ice-bath served for a 0° thermostat, and the water thermostat maintained a temperature of 24.96° constant to within 0.01°. The true temperatures were established by a calibrated thermometer whose ice-point was carefully checked. The constants of the cells were fixed by means of a solution of potassium chloride made up by weight to 0.019894 molar using the density data of Baxter,<sup>5</sup> and taking the conductivity of this solution as 0.002759 mhos at 24.96°. The constants were redetermined at the end of our measurements and found to be identical with the initial values. The slide-wire bridge could be read to one part in 5000 and was carefully calibrated under the conditions of its use. No readings were taken until the contents of the cells had reached precisely the temperature of the thermostat. Successive bridge readings were in most cases

<sup>2</sup> Jørgensen, *Z. anorg. Chem.*, **17**, 455-9 (1898).

<sup>3</sup> Lamb and Larson, *THIS JOURNAL*, **42**, 2025 (1920).

<sup>4</sup> Pfeiffer, *Ann.*, **346**, 59 (1906).

<sup>5</sup> Baxter *et al.*, *THIS JOURNAL*, **33**, 913 (1911).

constant to within the accuracy of a setting, and the mean of several readings was recorded.

In the case of the dinitro-tetrammine salts, however, a slow decrease in conductivity was noticeable at 25°, while with the carbonato-tetrammine this change was noticeable at 0° and so rapid at 25° as to make measurements of little value. In these latter cases the measurements were made over a period of 2 or 3 hours, and extrapolated to zero time.

### The Water Correction.

The correction of our conductivity measurements for the conductivity of the water is of considerable and unusual importance. This is due to the fact that the conductivity of the water, and indeed of any carefully purified water distilled in vessels open to the air is substantially that of the carbonic acid dissolved in it.<sup>6</sup> In acid or neutral solutions the corrections on this account are of no special importance, but here this carbonic acid will neutralize an equivalent quantity of the base and, as the net effect of this is to replace a swift, hydroxyl ion for a sluggish, carbonate ion, a considerable correction, at least in dilute solutions, must be applied. Calling  $C_{H_2CO_3}$  the total concentration of the carbonic acid, this correction will be

$$\Delta = \frac{2 \lambda_{OH^-} - \lambda_{CO_3^{--}}}{1000} C_{H_2CO_3}$$

where  $\lambda_{OH^-}$  and  $\lambda_{CO_3^{--}}$  are the conductivities of the hydroxyl and carbonate ions at the temperature of the measurements.

Since the specific conductivity of a solution of carbon dioxide is proportional to the square root of the partial pressure of carbon dioxide, and since carbon dioxide is only slightly dissociated even at these concentrations, the specific conductivity must also be proportional to the square root of its total concentration. A solution whose total concentration of carbon dioxide is  $2.94 \times 10^{-5}$  mols has a specific conductivity of  $0.65 \times 10^{-6}$  mhos at 0°.<sup>7</sup> Therefore, calling  $L_0$  the specific conductivity of the water at 0°,  $C_{H_2CO_3} = L_0^2 \frac{2.94 \times 10^{-5}}{0.65 \times 10^{-6}} = 6.8 \times 10^7 L_0^2$ ; and therefore  $\Delta_0 = 8.3 \times 10^6 L_0^2$ ; and  $\Delta_{25} = 2.82 \times 10^7 L_0^2$  mhos. These corrections at 0° and 25° have been applied to the specific conductivities at concentrations down to 0.00666 *M*, and since  $L_0$  varied between 0.94 and  $1.48 \times 10^{-6}$  mhos, the correction varied between 0.73 and  $1.8 \times 10^{-5}$  at 0° and 2.5 and  $6.2 \times 10^{-5}$  mhos at 25°.

This method of correction is rigorous enough at these concentrations. At still lower concentrations the question arises whether the second hydrogen of carbonic acid is sufficiently ionized to react completely with the hydroxyl ions.

<sup>6</sup> Kendall, *THIS JOURNAL*, 39, 7 (1917).

<sup>7</sup> Kendall, *ibid.*, 38, 1494-5 (1916).

If only the first hydrogen were neutralized the decrease in the specific conductivity would be<sup>8</sup>

$\Delta_{0}^{\circ} = (\lambda_{\text{OH}^-} - \lambda_{\text{HCO}_3^-})_0 \cdot C_{\text{H}_2\text{CO}_3} = 0.080 \text{ } C_{\text{H}_2\text{CO}_3} \text{ mhos}$ ; and similarly  $\Delta_{25}^{\circ} = 0.146 \text{ } C_{\text{H}_2\text{CO}_3} \text{ mhos}$ . If the second hydrogen were then neutralized, the further decrease would be  $\Delta_{0}^{\circ} = 0.042 \text{ } C_{\text{H}_2\text{CO}_3}$  and  $\Delta_{25}^{\circ} = 0.072 \text{ } C_{\text{H}_2\text{CO}_3}$ .

The extent to which these neutralizations will occur can be computed from the ionization constants of carbonic acid and of water. The ionization constant of the first hydrogen of carbonic acid is  $K_1 = 2.24 \times 10^{-7}$  at  $0^\circ$  and  $3.5 \times 10^{-7}$  at  $25^\circ$ ;<sup>9</sup> that of the second is  $K_2 = 6 \times 10^{-11}$  at  $18^\circ$ .<sup>10</sup> It is evident that at the concentration of hydroxyl ion under consideration ( $0.0001 \text{ } M$ ) the neutralization of the first hydrogen ion may be considered as complete.

The neutralization of the second hydrogen will be determined by the equilibrium equations

$$C_{\text{H}^+} \times C_{\text{OH}^-} = S_{\text{H}_2\text{O}}, \text{ and } \frac{C_{\text{H}^+} \times C_{\text{CO}_3^{--}}}{C_{\text{HCO}_3^-}} = K_2,$$

where  $S_{\text{H}_2\text{O}}$  represents the ion product of water. Calling  $C_{\text{OH}^-}$  the initial concentration of hydroxyl ion, that is, its concentration after the complete neutralization of the first hydrogen of carbonic acid,  $x$  the number of mols of the second hydrogen neutralized, and  $y$  the number of mols of carbonate ion formed at equilibrium,  $C_{\text{H}^+} = y - x$  and  $C_{\text{OH}^-} = C_{\text{OH}^-} - x$ . Then  $(y - x)(C_{\text{OH}^-} - x) = S_{\text{H}_2\text{O}}$ ; and  $(y - x)y = K_2(C_{\text{H}_2\text{CO}_3 - x})$ .

The solution of these two equations gives a third degree equation. It is therefore much simpler to solve them by a process of approximation for each set of values of the constants, first guessing a value of  $y$ , then solving each equation for  $x$ , and finally varying  $y$  until each equation gives an identical value for  $x$ . After a few trials this solution can be made very rapidly. Values of  $y$  computed in this way for  $C_{\text{H}_2\text{CO}_3} = 1.18 \times 10^{-4} \text{ } M$ , and for a series of hydroxyl-ion concentrations at  $25^\circ$  are given in Table I. These values of  $y$  divided by  $C_{\text{H}_2\text{CO}_3}$  give the fraction of the total carbonic acid converted into the carbonate ion; that is, the fraction fully neutralized. The resulting figures are entered in the fourth column of Table I. Similar computations were made for the other concentrations

<sup>8</sup> For the conductivity of  $\text{HCO}_3^-$  see Kendall, *THIS JOURNAL*, 38, 1489 (1916).

<sup>9</sup> Kendall, *ibid.*, 38, 1486 (1916).

<sup>10</sup> Johnston, *ibid.*, 37, 2004 (1915).

McCoy, *Am. Chem. J.*, 29, 437 (1903).

Walker and Cormack, *J. Chem. Soc.*, 77, 8 (1900).

Shields, *Z. physik. Chem.*, 12, 167 (1893).

Auerbach and Pick, *Arbeiten kais. Gesundheitsamt.*, 38, 243 (1911).

Prideaux, *Proc. Roy. Soc.*, 91A, 535 (1915).

of carbonic acid. Values for intermediate concentrations of hydroxyl ions were found by graphical interpolation.

TABLE I.  
ION CONCENTRATIONS.  
[ $\text{CH}_3\text{CO}_2 = 1.18 \times 10^{-4}$ . Temperature =  $25^\circ$ .]

Initial conc. $\text{OH}^- \times 10^3 M.$	$\text{CO}_3^{--} \times 10^3 M.$	$\text{CO}_2^{--} \text{ or } \gamma \times 10^3$	$\frac{\text{CO}_3^{--}}{\text{CH}_3\text{CO}_2}$
6.67	6.54	0.115	0.97
1.33	1.21	0.103	0.87
0.667	0.549	0.087	0.74
0.218	0.100	0.033	0.28
0.133	0.016	0.0064	0.055

It can be seen from this table that the neutralization is nearly complete at the highest concentrations, and corrections for this effect were therefore only applied at concentrations of  $0.0013 M$  and below. With water of the purity used ( $L_0 = 0.9 - 1.4 \times 10^{-6}$  mhos) the total correction for water is, however, very large at the lowest concentration, so that any correction is unsatisfactory. This is shown by the large values of the water correction expressed as percentages of the total conductivity ( $\Delta/L$ ) in the tables of data. In any attempt to secure more accurate values for low concentrations much purer water should be used.

**Correction for the Solubility of Silver Oxide.**—During trituration of the cobaltamine bromide with silver oxide, and the subsequent washing some silver must dissolve, and thus contaminate the solution of the cobaltamine hydroxide. The amount of this contamination can be determined from the known solubility of silver oxide.

The total solubility of silver hydroxide is  $2.16 \times 10^{-4}$  mols per liter at  $25^\circ$ , according to the careful and direct measurements of Noyes and Kohr.<sup>11</sup> The ion concentration of the saturated solution is  $1.23$  and  $1.39 \times 10^{-4}$  mols at  $20^\circ$  and  $25^\circ$ , respectively, according to Böttger.<sup>12</sup> Assuming that the total solubility has the same temperature coefficient as the ion concentration, it will equal  $8 \times 10^{-5}$  mols at  $0^\circ$ . The total volume of water used during trituration and washing may be taken as  $50$  cc., and

<sup>11</sup> Noyes and Kohr, *Z. physik. Chem.*, **42**, 338 (1903).

<sup>12</sup> Böttger, *Z. physik. Chem.*, **46**, 602 (1903). It should be pointed out that Böttger's values are somewhat too large for silver hydroxide and lead hydroxide, as he corrected the conductivity of their solutions by simply subtracting the conductivity of the water. This neglects the fact that the carbonic acid which is chiefly responsible for the conductivity of the water will have its first hydrogen completely neutralized, and will therefore have a higher conductivity than when slightly dissociated in the original water. The correction,  $\Delta'$ , for this effect will evidently be

$$\text{CH}_3\text{CO}_2 \frac{(\lambda_{\text{Ag}^+} + \lambda_{\text{OH}^-})}{1000} \text{ or } 0.11 \text{ CH}_3\text{CO}_2.$$
 For the water which he used  $\text{CH}_3\text{CO}_2 = 2.8 \times 10^{-5}$ , and therefore  $\Delta'_{25^\circ} = 3.1 \times 10^{-6}$  and  $\Delta'_{20^\circ} = 2.8 \times 10^{-6}$  mhos. These corrections, applied to Böttger's values for the ion concentration give, for  $25^\circ$  and  $20^\circ$ , respectively,  $1.39$  and  $1.23 \times 10^{-4} M$ .

assuming its complete saturation and the complete dissociation of the silver hydroxide, the concentration of silver ion would be  $1.6 \times 10^{-5} M$ . This amount of contamination is wholly negligible in the  $3300 \times 10^{-5} M$  solutions which were chiefly studied, and practically negligible in the few  $330 \times 10^{-5} M$  solutions. No correction has, therefore, been applied to our results for this effect.

### The Conductivity Data.

The conductivity data are collected in the following tables.  $\lambda$  and  $\alpha$  signify molecular conductivity and percentage dissociation as usual,  $L_0$ , the specific conductivity at  $0^\circ$  of the water used;  $\Delta/L$ , the percentage of the total conductivity which the water correction represents at the various concentrations, and  $R$  the molecular conductivity of the hydroxide obtained by subtracting the conductivity of the neutral salt from the observed values.

TABLE II.  
HEXAMMINE COBALTIC BROMIDE.  
 $L_0 = 1.35 \times 10^{-6}$  mhos.

Conc. $M \times 10^4$ .	$\lambda_{0^\circ}$ .				$\alpha_{0^\circ}$ .		$\lambda_{25^\circ}$ .				$\alpha_{25^\circ}$ .	
	1.	Observed. 2.	Mean.	Calc. $\kappa=1.43$ .	%.		1.	Observed. 2.	Mean.	Calc. $\kappa=1.45$ .	%.	
33.23	174.1	174.1	174.1	173.3	58.6	319.1	319.1	319.1	319.9	57.6		
6.662	215.3	215.2	215.3	217.4	72.5	397.0	397.0	397.0	397.9	77.1		
1.336	253.8	253.8	253.7	251.0	85.4	462.0	461.8	461.9	460.1	83.4		
0.2678	272.1	272.1	272.1	273.1	91.6	502.6	502.4	502.5	502.2	90.6		
0				(297.1)					(553.5)			

TABLE III.  
HEXAMMINE COBALTIC DIBROMIDE HYDROXIDE. HEXAMMINE COBALTIC BROMIDE  
DIHYDROXIDE.  
 $L_0 = 1.48 \times 10^{-6}$  mhos.

Conc. $M \times 10^4$ .	$\lambda$ .		$R$ .		$\alpha$ .		$\lambda$ .		$R$ .		$\alpha$ .	
	0°.	25°.	0°.	25°.	0°.	25°.	0°.	25°.	0°.	25°.	0°.	25°.
33.23	216.9	388.4	101	175	63	58	258.2	449.4	200	343	63	57
6.662	259.5	463.8	116	199	72	66	302.3	529.0	230	397	72	66
1.336	293.8	528.8	125	221	78	73	344.0	603.4	260	448	81	74
0.2678	333.6	621.0	152	286	95	95	387.2	693.2	296	526	93	87
0												

TABLE IV.  
HEXAMMINE COBALTIC HYDROXIDE.  
 $L_0 = 1.48 \times 10^{-6}$  mhos.

Conc. $M \times 10^4$ .	$\lambda_{0^\circ}$ mhos.		$\alpha_{0^\circ}$ .	$\lambda_{25^\circ}$ mhos.		$\alpha_{0^\circ}$ .	$\Delta/L$ .
	Obs.	Calc. $\kappa=1.4$ .		Obs.	Calc. $\kappa=1.3$ .		
33.23	347.5	347.5	72.2	591.3	589.9	65.5	0.2
6.662	396.9	396.8	82.4	675.3	672.7	74.8	0.7
1.336	431.1	431.6	89.5	739.0	741.8	81.8	3.2
0.2678	469.0	450.7	97.4	843.0	791.8	93.4	14.0
0		(482.0)			(901.0)		

TABLE V.  
AQUO-PENTAMMINE COBALTIC HYDROXIDE.  
 $L_0 = 1.31 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	Obs. $\lambda_0^\circ$ mhos.	Calc. $n=1.11$	$\alpha_0^\circ$ %	$\alpha'_0^\circ$ %	$\Delta/L$ %
33.21	223.4	223.9	45.7	70.8	0.2
6.66	244.7	244.6	50.0	77.9	1.1
1.335	261.8	265.5	53.5	82.9	4.1
0.2683	286.8	285.7	58.6	90.7	17.5
0		(475.0)			

TABLE VI.  
DIAQUO-TETRAMMINE COBALTIC HYDROXIDE.  
 $L_0 = 1.04 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	$\lambda_0^\circ$ mhos.	$\alpha_0^\circ$ %	$\alpha'_0^\circ$ %	$\Delta/L$ %
6.59	116.4	24.8	74.7	2.5
1.321	115.4	24.6	74.0	6.0
0.265	102.7	21.8	65.9	31.3
0	(469.0)			

TABLE VII.  
TRIETHYLENEDIAMINE COBALTIC HYDROXIDE.  
 $L_0 = 1.34 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	$\lambda_0^\circ$ mhos.		$\alpha_0^\circ$ %	$\lambda_{25}^\circ$ mhos.		$\alpha_{25}^\circ$ %	$\Delta/L$ %
	Obs.	Calc. $n=1.37$		Obs.	Calc. $n=1.35$		
33.29	304.2	303.0	67.0	519.1	512.3	66.4	0.2
6.674	344.0	344.5	81.2	596.4	594.5	76.3	0.7
1.338	375.4	374.5	88.6	651.6	659.6	83.3	2.8
0.2683	394.4	394.6	93.1	706.8	705.5	90.4	12.7
0		(423.6)			(781.0)		

TABLE VIII.  
DIAQUO-DIETHYLENEDIAMINE COBALTIC HYDROXIDE.  
 $L_0 = 1.34 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	$\lambda_0^\circ$ mhos.	$\alpha_0^\circ$ %	$\alpha'_0^\circ$ %	$\lambda_{25}^\circ$ mhos.	$\alpha_{25}^\circ$ %	$\Delta/L$ %
33.29	107.6	24.6	73.7	185.0	22.7	0.4
6.674	113.9	26.6	79.8	197.4	25.2	2.0
1.338	116.8	27.3	81.8	209.0	26.7	9.0
0.2683	143.1	33.4	100.3	269.4	34.5	33.5
0	(430.0)			(778.5)		

TABLE IX.  
CARBONATO-TETRAMMINE COBALTIC HYDROXIDE.  
 $L_0 = 1.04 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	$\lambda_0^\circ$ mhos.	$\alpha_0^\circ$ %	$\Delta/L$ %
33.32	108.7	89.2	0.3
6.674	113.4	93.1	
1.338	119.0	97.6	5.7
0.2683	100.3	85.3	24.0
0	(121.8)		

TABLE X.  
1,2-DINITRO-TETRAMMINE COBALTIC HYDROXIDE.  
 $L_0 = 0.94 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	$\lambda_{0^\circ}$ mhos.	$\alpha_{0^\circ}$ %.	$\lambda_{25^\circ}$ mhos.	$\alpha_{25^\circ}$ %.	$\Delta/L$ %.
6.657	102.5	83.3	176.8	79.2	1.1
1.335	99.9	81.2	179.0	78.4	5.4
0.2676	102.8	84.7	201.8	89.4	21.0
0	(123.1)		(228.3)		

TABLE XI.  
1,6-DINITRO-TETRAMMINE COBALTIC HYDROXIDE.  
 $L_0 = 0.94 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	$\lambda_{0^\circ}$ mhos.	$\alpha_{0^\circ}$ %.	$\lambda_{25^\circ}$ mhos.	$\alpha_{25^\circ}$ %.	$\Delta/L$ %.
3.329	116.2	94.6	201.4	88.3	1.9
0.6675	117.2	95.4	209.0	91.6	9.0
0.1339	123.2	100.3	256.0	112.2	30.3
0	(122.9)		(228.1)		

TABLE XII.  
DINITRO-AQUO-TRIAMMINE COBALTIC HYDROXIDE.  
 $L_0 = 0.94 \times 10^{-6}$  mhos.

Conc. $M \times 10^3$	$\lambda_{0^\circ}$ mhos.	$\alpha_{0^\circ}$ %.	$\lambda_{25^\circ}$ mhos.	$\alpha_{25^\circ}$ %.	$\Delta/L$ %.
5.413	52.4	39.0	92.1	37.0	5.4
1.085	48.6	36.0	90.2	36.0	13.7
0.2176	54.2	40.0	120.0	48.0	48.0
0	(134.5)		(251.6)		

In view of Werner's conclusion<sup>13</sup> that in alkaline solutions of the amines *hydroxo* compounds are present in equilibrium with the aquo hydroxide we have computed from the observed conductivities of all the aquo hydroxides the percentage ionization of the remaining hydroxide, assuming that all of the complexly bound water has been replaced by hydroxyl groups. The results obtained are collected in the columns headed  $\alpha'_{0^\circ}$  in the above tables.

#### The Conductivities at Zero Concentration.

The conductivities at zero concentration, required to compute the degree of ionization, can, in the case of the most highly ionized bases, be computed with considerable certainty from the actually observed conductivities; but in other cases and in general, on account of the serious effect of dissolved carbonic acid on conductivity measurements of bases, it is advantageous to compute these conductivities from measurements of the conductivities of salts of these bases. This is the method we have adopted. In most cases the necessary data were found in the literature. The values adopted for the conductivities of the various anions used in these com-

<sup>13</sup> Werner, Ref. 1, p. 264.

putations,<sup>14</sup> and the resulting conductivities of the various cobaltammine ions are collected in Table XIII.

TABLE XIII.  
CONDUCTIVITIES OF THE VARIOUS COBALTAMMINE IONS.

Cobaltammine cations.	$\lambda$ .		Anions.	$\lambda$ .	
	0°. mhos.	25°. mhos.		0°. mhos.	25°. mhos.
$[\text{Co}(\text{NH}_3)_6]^{+++}$	167.0	327.0	$\text{Br}^-$	43.1	75.6
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+++}$	160.0	314.0	$\text{Cl}^-$	41.1	75.5
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++}$	154.0	300.0	$\text{OH}^-$	105.0	192.0
$[\text{Co}(\text{en})_3]^{+++}$	108.6	205.5	$\text{NO}_3^-$	40.4	70.6
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{+++}$	115.0	219.0	$\text{HCO}_3^-$	25.0	46.2
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$	16.8	33.8	$\text{CO}_3^{=}$	88.0	166.4
$1,2\text{-}[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	18.1	36.3			
$1,6\text{-}[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	17.9	36.1			
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})(\text{NO}_2)_2]^+$	29.5	59.6			

*Hexammine Cobaltic Ion.*—Although numerous measurements of the conductivity of hexammine salts have been made by Werner and Miolati<sup>15</sup> and Werner and Herty,<sup>16</sup> the results are discordant and much lower than those obtained more recently for the chloride by Harkins, Hall and Roberts.<sup>17</sup> We have, therefore, measured the conductivity of hexammine bromide at both 0° and 25°, and the results are collected in Table II. Values for the conductivity at zero concentration have been obtained by the well-known method,<sup>18</sup> based on the Storch-Bancroft equation, of plotting  $1/\lambda$  against  $(C\lambda)^{n-1}$  and varying  $n$  until the points lie as closely as possible to a straight line. The values of the exponent and the limiting conductivities thus obtained and of the molar conductivities computed inversely from them are included in the table. The close agreement of the computed and observed conductivities indicates the probable reliability of the extrapolation. The data of Harkins, Hall and Roberts on the chloride have been computed in a similar fashion; satisfactory concordance was obtained using  $n=1.50$  and  $1.48$  at 0° and 25°, respectively; giving 165.2 and 326.7 mhos for the conductivity of the hexammine ion, as compared with the 167.8 and 327.3 mhos which we obtained above from our measurements on the bromide. We have, therefore, adopted 167 and 327 mhos for our further computations. The reliability of these values is further attested by the close agreement of the conductivities of the hydroxide computed from them with the observed conductivities (Table IV).

<sup>14</sup> See Johnston, *THIS JOURNAL*, 31, 1015 (1909); and Landolt u. Börnstein, "Tabellen."

<sup>15</sup> Werner and Miolati, *Z. physik. Chem.*, 12, 41 (1893); 14, 511 (1894); 21, 237 (1896).

<sup>16</sup> Werner and Herty, *Z. physik. Chem.*, 38, 336 (1901).

<sup>17</sup> Harkins, Hall and Roberts, *THIS JOURNAL*, 38, 2656 (1916).

<sup>18</sup> See Noyes and Coolidge, *Carnegie Inst.*, Pub., 63, p. 50.



*Aquo-pentammine and Diaquo-tetrammine Ions.*—The conductivities of various salts of these ions have been measured at 25° by Werner and Miolati.<sup>19</sup> These measurements have shown that the aquo-pentammine and the diaquo-tetrammine salts have conductivities 12 and 25 mhos smaller than the hexammine ion at 0.0005 *M* concentration. We have, therefore, adopted 160 and 154 at 0° and 314 and 300 mhos at 25° for these values.

*Triethylenediamine Cobaltic Ion.*—The conductivities of the chloride and nitrate of this ion have been measured at 25° by Werner and Hertz.<sup>16</sup> Their measurements, extrapolated to zero concentration in the usual way give 196 and 214 mhos, respectively, for the conductivity of the triethylenediamine ion. We have adopted the mean of these results, namely 205.5 mhos. This value is confirmed by the close agreement of the conductivities of the hydroxide computed from it with the observed conductivities. No measurements of the conductivities of these salts at zero degrees have been found in the literature; we have, therefore, adopted the value 108.6 mhos, computed from the conductivity of the hydroxide at zero concentration (423.6 mhos) found by direct extrapolation. The approximate, at least, correctness of the result is confirmed by the close agreement of the temperature coefficient, derived from it, and the known value at 25°, (0.0357) with the similar coefficients of the hexammine, aquo-pentammine and diaquo-tetrammine ions, namely 0.0384, 0.0364 and 0.0360.

*Diaquo-diethylenediamine Ion.*—No measurements of the conductivities of the salts of this ion have been made, nor are our measurements of the conductivity of the hydroxide at different concentrations sufficiently concordant to permit extrapolation. We have, therefore, merely estimated the conductivity of this ion by assuming that the replacement of 4 ammonia groups in diaquo-tetrammine will produce the same change per mol. of ammonia as when all 6 ammonia groups are replaced in the hexammine to form the triethylenediamine ion. On this basis the conductivity becomes 115 at 0° and 219 mhos at 25°.

*Carbonato-tetrammine Cobaltic Ion.*—The conductivity of this ion at 25° was determined by extrapolation, taking  $n=1.33$ , of the conductivity data on the nitrate obtained by Werner and Miolati.<sup>20</sup> The value thus obtained, 33.8 mhos, is only a few per cent. less than the corresponding value for the closely related 1,2-dinitro-tetrammine ion at the same temperature. We have assumed that the values at zero degrees will bear the same proportionate relation. This gives the conductivity of the carbonato ion as 16.8 mhos.

*1,2- and 1,6-Dinitro-tetrammine Ions.*—The conductivities of these ions

<sup>19</sup> Werner and Miolati, *Z. physik. Chem.*, 12, 42 (1893); 14, 520 (1894); and 21, 237 (1896).

<sup>20</sup> Werner and Miolati, *Z. physik. Chem.*, 21, 234 (1896).

have been obtained by extrapolation of the measurements of Harkins, Hall and Roberts<sup>17</sup> on the nitrate and chloride. The exponent  $n$  was found to be 1.4 for the 1,2-dinitro nitrate and 1.5 for the 1,6-dinitro chloride, giving 18.1 and 17.9 at 0°, and 36.3 and 36.1 mhos at 25° for the 1,2- and 1,6-dinitro ions, respectively.

*Dinitro-aquo-triammine Ion.*—The conductivity of this ion at 25° has been computed by extrapolation of the measurements of Werner and Miolati<sup>21</sup> on the chloride, taking  $n=1.40$ , as 59.6 mhos. The value at 0° was found, as in the case of the carbonato, by comparison with the 1,2-dinitro ion, giving the value 29.5 mhos.

### The Degrees of Ionization.

The degrees of ionization, computed for the different concentrations in the usual way, are included in the columns headed  $\alpha_0^\circ$  or  $\alpha_{25}^\circ$  of the above tables (II–XII). To facilitate comparison the values for 0.00133  $M$  have been collected in the following table (XIV). This concentration rather than the most dilute has been selected because it is not so subject to the uncertainties involved in the water correction.

TABLE XIV.

THE PERCENTAGE IONIZATION OF THE COBALTAMMINE BASES AT 0° AND 0.00133  $M$ .

Base.	$\alpha$ %.	$\alpha'$ %.
$[\text{Co}(\text{NH}_3)_6]^{+++}$	89.5	
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{+++}$	53.5	82.9
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++}$	24.6	74.0
$[\text{Co}(\text{en})_3]^{+++}$	88.6	
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{+++}$	27.3	81.8
$[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$	97.6	
1,2- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	81.2	
1,6- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	95.0	
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})(\text{NO}_2)_2]^+$	36.0	

These results bring out clearly the following facts.

(1) These bases are very strong. The univalent bases, carbonato-1,2- and 1,6-dinitro hydroxide, are quite as highly dissociated as the alkali hydroxides, while the hexammine and triethylenediamine hydroxides have no parallels among the simple tri-acid inorganic bases as regards solubility and extent of ionization.

(2) The replacement of ammonia by ethylenediamine has no noticeable effect on the extent of ionization. Thus, the hexammine and triethylenediamine, on the one hand, and the diaquo-tetrammine and the diaquo-diethylenediamine on the other, show almost identical ionization.

(3) The replacement of ammonia or ethylenediamine by water produces a marked decrease in the degree of ionization. This is apparent on com-

<sup>21</sup> Werner and Miolati, *Z. physik. Chem.*, 12, 46 (1893); and 21, 228 and 234 (1896).

paring hexamine with aquo-pentamine and diaquo-pentamine, triethylenediamine with diaquo-ethylenediamine, and the dinitro-tetramine with dinitro-aquo-triammine. The magnitude of the change is also substantially the same, per water molecule, in each case.

(4) The substitution of acido groups for ammonia or ethylenediamine has no marked effect on the ionization; the carbonato and 1,6-dinitro appear slightly more, the 1,2-dinitro slightly less ionized than the original unsubstituted ammine. It certainly does not produce the weak base which might perhaps be expected from the usual conceptions of organic chemistry. But it must be remembered that the mere decrease in valence, such as any complexly bound acido group would produce, would tend to favor the ionization of the hydroxyl group attached by a polar valence. What little effect there is on the ionization, if it is real, would indicate that the weakest acido group ( $\text{CO}_3$ ) gave the strongest base, as would be expected. This flatly contradicts Werner's qualitative conclusions and seriously invalidates his discussion of the theory of bases.

(5) The ionization of the 1,2-dinitro- is decidedly less than that of the 1,6-dinitro-tetrammine hydroxide. This agrees with Werner's qualitative estimate.<sup>22</sup>

(6) The values of  $\alpha'_0$  are in all cases possible; that is, the assumption that *all* the complexly bound water is replaced by hydroxyl groups does not lead to values of  $\alpha'_0$  greater than 100, though, of course, this does not *prove* that any such replacement has indeed taken place.

### The Relative Ionization of the Successive Hydroxyl Groups of Hexamine Cobaltic Hydroxide.

It appeared of interest to ascertain whether there is any marked difference in the degrees of ionization of the successive hydroxyl groups of the hexamine cobaltic hydroxide. This was tested not very conclusively by tritulating, in one case, one-third of the requisite quantity of the hexamine bromide with silver oxide as above described, and adding the resulting solution to a solution of the remaining two-thirds; in another case, the proportions were reversed. From the observed molecular conductivity  $2/3$  or  $1/3$  of the conductivity of the hexamine bromide was subtracted, the remainder, given in the columns headed *R*, presumably representing the conductivity of the hydroxide. These values divided by the conductivity of the uni- or di-hydroxide at infinite dilution give the percentage ionization ( $\alpha$ ). These results are collected in Table III, above. They indicate no marked difference for the three hydroxyl groups.

### Werner's Theory of Bases.

As mentioned at the beginning of this article Werner has proposed a

<sup>22</sup> Werner, Ref. 1, p. 265.

theory of bases and of hydrolysis founded largely on considerations connected with the cobaltammine hydroxides. This theory has apparently found such scant acceptance that only a brief discussion of it, and of the bearing of our observations upon it is required. It had its origin in the discovery by Pfeiffer among the amines of chromium, and later by Werner among the amines of cobalt and other metals, of the *hydroxo-ammine* salts. These substances, formed by salting out ammoniacal solutions of certain amines, appear to contain a complexly bound hydroxyl group. Dissolved in strong acids they give solutions from which ordinary aquo salts can be isolated, while with carbon dioxide they yield carbonato salts. On this specific, and on other general evidence, Werner concludes that all bases may be divided into two classes, "anhydro" and "aquo" bases. Ordinary metallic hydroxides, such as sodium, calcium, and aluminum hydroxides, ammonia and the hydroxo-ammines are anhydro bases; while aqueous solutions of these substances contain aquo bases, in equilibrium with the anhydro bases. Only the aquo bases are ionized. Finally, neutralization, according to Werner, is not the simple union of a hydrogen ion with an hydroxyl ion, but the addition of hydrogen ion to the hydroxo group of the anhydro base.

Examined carefully there appear to be two separate and novel hypotheses in this theory. The first is that the hydroxyl group in the free base is complexly bound and must be replaced by a water (or solvate) molecule before ionization can occur. The view that ionization is due to the combination of the solvent with the solute or to the loosening of the bonds of the solute by the residual valences of the solvent, as it is variously expressed, is an old, widespread and multiform theory. Werner's modification simply is that a stoichiometric relation always exists, one molecule of water actually replacing the hydroxyl group. The water then becomes complexly bound, while the hydroxyl group is now held only by polar valences and will therefore dissociate.

Now while this precise replacement of the *acido* group by the water molecule does indeed occur in the slow ionization of chloro-pentammine cobalt chloride and similar compounds, and presumably also occurs in the ionization of hydroxo compounds, and while it might also occur with a metallic hydroxide which forms a hydrate containing precisely one molecule of water for each hydroxyl group, it is a gratuitous and arbitrary assumption not only in the case of amines such as the hexamine, the dinitro-tetrammine, etc., for which no hydroxo base and no aquo compounds corresponding to the hydroxo base have been found, but also in the case of metallic hydroxides which either do not form hydrates at all or form them containing more than one molecule of water per hydroxyl group. Thus, for instance, in the case of the hexamine base Werner would have to assume the existence of the particular ion,

$[\text{Co}(\text{NH}_3)_6(\text{H}_2\text{O})_3]^{+++}$ , for which there is to our knowledge no evidence whatever.<sup>23</sup> A more probable view would be that acido groups, including the hydroxyl group, may or may not be held complexly, that is, by non-polar bonds. If held complexly, they will not be ionized until displaced by a solvate or other neutral molecule. If not held complexly, that is, if held by electrostatic or polar valence, they will ionize at once up to an equilibrium condition, when dissolved in a suitable solvent. The ionization in each case is presumably brought about by the chemical interaction of the solute and solvent, but how definite the compositions of the resulting compounds or solvated ions are is an open question. Presumably there is a quite definite and fixed orientation of at least a few molecules of the solvent about each ion.

The second novel feature of this theory is that neutralization occurs, not by the direct combination of hydrogen ions with hydroxyl ions, but by the addition of a hydrogen ion to the complexly bound hydroxyl group of the anhydro base. That is, instead of imagining that water is first formed, the equilibrium between aquo and anhydro bases upset and hydroxo thus converted into aquo base, Werner prefers to imagine substantially the reverse procedure. The hydrogen ion, adding to the hydroxo-ammine ion, forms the aquo ion directly; this causes the re-formation of more hydroxo-ammine ion from the aquo ion with the liberation of water and the binding of the hydroxyl ion. There is no direct evidence in support of this inverted picture. It must lead to the same equilibrium conditions as the usual interpretation, and it seems unlikely that hydrogen ion would add rapidly to an hydroxo group, but not at all to an hydroxyl ion bearing an opposite electric charge.

The only evidence which Werner presents in support of this radical proposal is that hydroxo-nitro-tetrammine and hydroxo-dinitro-tetrammine react more strongly basic in solution than do the corresponding hydroxo-pentammine and hydroxo-aquo-tetrammine salts, which is the opposite to what would be expected from the usual point of view. This could, however, be predicted from his theory because, he alleges somewhat darkly, the acido group would increase the affinity of the complex hydroxyl group for the hydrogen ion.

Our measurements do show that dinitro-tetrammine is indeed stronger than diaquo-tetrammine hydroxide. But, in the first place, as indicated above, these comparisons between bases of different valences, or acidities, to use the older term, are not justifiable, for it is recognized that, other things being equal, mono-acid bases will be stronger than di-acid bases and very much stronger than tri-acid bases. In the second place, these comparisons are between nitro and aquo groups; if similar comparisons

<sup>23</sup> The nearest approach to such evidence is that hydrates of hexamine chloride containing 3 molecules of water have been prepared.

are made between nitro and ammonia or ethylenediamine groups the result is wholly different. In spite of the handicap of greater acidity (valence) there is no significant difference in their strengths; dinitro-tetrammine, hexammine, and triethylenediamine hydroxides exhibit practically the same ionization. What little difference there is accords with the usual interpretation; thus, as pointed out above, carbonato-tetrammine hydroxide is a stronger base than the stereochemically similar 1,2-dinitro-tetrammine hydroxide. Finally, it should be pointed out in this connection that the marked decrease in the strength of the bases produced by the replacement of ammonia and ethylenediamine by water, the outstanding result of our measurements, is also in accord with the usual views.

Summarizing regarding this theory we would say that, while it may well be true that any complexly bound hydroxyl group, or acido group, must first be replaced by a water molecule before ionization can occur, it is improbable that this is a necessary or sufficient mechanism for all ionization; nor can the idea that neutralization takes place exclusively by addition of the hydrogen ion to a hydroxo group be seriously entertained.

### Summary.

(1) The strengths of 9 cobaltammine bases have been determined by measuring their conductivities over a range of concentrations in dilute solutions and comparing these with the conductivities at zero concentration, as computed from measurements of the conductivities of salts derived from these bases.

(2) The determinations have shown (*a*) that these bases are very strong, certain of them are as highly ionized as the alkali hydroxides; (*b*) that the replacement of ammonia by ethylenediamine has no noticeable effect; (*c*) that the replacement by water molecules produces a marked and progressive decrease in the strength; (*d*) that the substitution of acido groups has no marked effect on the strength, the electrostatic effect of a decrease in valence perhaps offsetting the chemical effect of the acid radical; the stronger acid radical produced the weaker base; (*e*) that there is no marked difference in the ionization of the successive hydroxyl groups in hexammine cobalt hydroxide.

(3) The improbability of the distinctive features of Werner's theory of bases has been brought out, and a more probable interpretation suggested.

(4) Equations giving the important correction of the conductivity of solutions of bases for the conductivity of the carbon dioxide dissolved in the water have been derived and applied.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF QUEENSLAND.]

## SUBSALTS OF BISMUTH.

BY HENRY GEORGE DENHAM.

Received July 22, 1921.

The successful preparation of various subsalts of lead by the action of the vapor of methyl iodide upon lead suboxide<sup>1</sup> has suggested that this method might also lead to definite results, if applied to the suboxides of other elements, *e. g.*, bismuth.<sup>2</sup> Moreover, it has already been established by the author<sup>3</sup> that salts of bismuth, of a lower stage of oxidation than the trivalent, can exist in aqueous solution.

## Preparation of Bismuth Suboxide.

Bismuth suboxide ( $\text{BiO}$ ) has been described by various workers<sup>4</sup> but it was Tanatar who first brought forward definite evidence of the chemical identity of this substance, his work being subsequently confirmed by Herz and Guthmann.<sup>5</sup> In the following work a slight modification of Tanatar's method was introduced.

The basic oxalate of bismuth, prepared according to Tanatar's method,<sup>2</sup> was decomposed in the apparatus already used by the author for the preparation of lead suboxide and subsalts.<sup>3</sup> With the aid of a 3-fall Sprengel pump for removing the gases formed during the decomposition, about 2 g. of oxalate could be converted into the suboxide in 6 to 8 hours at 250–260°. The suboxide retained small quantities of carbon dioxide very tenaciously, while at very low pressures the suboxide shows a tendency to lose oxygen. This is borne out in the following experiments.

Temperature, ° C.....	260	270	265	260	265	265
Duration of the decomp., hours..	8	10	10	18	36	48
Bi, %.....	90.7	91.7	91.8	93.1	95.3	95.5

Bi in  $\text{BiO}$ , calc. = 92.8%.

In making the suboxide as a preliminary step in the preparation of bismuth subsalts, the decomposition was never allowed to proceed longer than 8 hours, nor was the pressure allowed to fall sufficiently low to cause the removal of oxygen. The traces of carbon dioxide left behind in the suboxide were found to be completely eliminated during the subsequent treatment with the vapor of methyl iodide.

It is noteworthy that all samples prepared in this way were spontaneously oxidized on exposure to the air except those which approached pure bismuth in composition.<sup>2,3</sup>

## Preparation of Bismuth Subsals.

About 2 g. of the basic oxalate was mixed with about 4 times its weight of silica or of powdered glass, not too fine in grain. This was necessary

<sup>1</sup> *J. Chem. Soc.*, 111, 29 (1917); 113, 249 (1918); 115, 109 (1919).<sup>2</sup> Tanatar, *Z. anorg. Chem.*, 27, 437 (1901).<sup>3</sup> Denham, *J. Chem. Soc.*, 93, 835 (1908).<sup>4</sup> Schneider, *Pogg. Ann.*, 96, 130 (1855). Heinz, *ibid.*, 63, 55 (1844).Weber, *ibid.*, 107, 596 (1859). Berthelot, *J. Pharm.*, 14, 616 (1829).<sup>5</sup> Herz and Guthmann, *Z. anorg. Chem.*, 53, 64 (1907).

to prevent caking, and not to keep down the temperature of the reaction as in the case of lead subiodide already described.<sup>1</sup> The apparatus used in the preparation of the subsalts of lead was again adopted without alteration, nor did any material change in the method of procedure prove necessary. After the formation of an approximately pure suboxide, about 10 cc. of pure methyl iodide was introduced into the distillation vessel, and the distillation begun at a temperature of 260–262°. Extreme difficulty was experienced in bringing the reaction between methyl iodide and the suboxide to completion. Generally, after an hour's distillation the evolution of gas entirely ceased. This should indicate that the reaction is at an end, but examination of the cooled reaction vessel showed that in nearly all cases the reaction was incomplete at this stage, the product being dark red and obviously heterogeneous. A further distillation at the original temperature gave a renewed evolution of gas, this often lasting another hour. In order to take advantage of this renewed reactivity conferred upon the reaction mixture by cooling, the distillation was carried out in two stages. Five cc. of methyl iodide was distilled through the suboxide at 260–262°, the duration of the distillation being about an hour. The reaction vessel was then cooled to room temperature, and then slowly raised again to the original temperature of distillation. An additional 5 cc. was then distilled through the reaction mixture. In some cases it was necessary to subject the reaction mixture to a yet further distillation. As it had already been established that at temperatures above 262° methyl iodide oxidizes lead subiodide<sup>1</sup> to the normal iodide, no distillation tests were carried out above this temperature. At the completion of the distillation, the distillate was cooled by liquid ammonia, the apparatus partly evacuated, the vessel containing the distillate sealed off, and the apparatus completely evacuated by means of the Sprengel pump.

**Products of the Reaction.**—As a result of the distillation the following products were isolated. (1) The reaction vessel contained roughly 2 g. of a non-volatile, brick-red powder which appeared perfectly homogeneous under the microscope. (2) Just outside the oven there appeared bright red crystals of considerable volatility. (3) The distillate was yellow whereas in the corresponding case of lead subiodide it was colorless. On admitting air into the distillate a pale yellow solid separated, the methyl iodide at the same time decolorizing.

**The Product in the Reaction Vessel.**—This non-volatile, brick-red substance was found to be perfectly stable in dry air. Analysis of this compound gave the following results.

These results agree closely with the calculated percentages for the basic subiodide,  $2\text{BiI}_2 \cdot 3\text{BiO}$ . It is of interest at this stage to note that the distillation of methyl iodide over bismuth trioxide under similar conditions leads to the formation of bismuth oxyiodide, a reddish compound, the



	Bi. %.	I. %.	O (by difference). %.
	64.9	31.3	3.8
	64.8	31.7	3.5
	65.2	31.7	3.1
	64.8	31.9	3.3
	65.0	31.5	3.5
Mean	64.9	31.6	3.5
Calc.	64.9	31.8	3.3

analysis of which indicates the formula  $\text{BiOI}$  or  $\text{BiI}_3\cdot\text{Bi}_2\text{O}_3$ . The percentage of bismuth in 2 samples of this oxyiodide was found to be 58.96 and 59.00 (calc. 59.28).

Bismuth sub-oxyiodide is non-volatile even at  $300^\circ$ . On being heated in the absence of air to a temperature of  $350^\circ$  and above, the reddish subsalt becomes dark and patchy, and does not regain its former homogeneity on cooling. Presumably, decomposition into metal and a basic tri-iodide has occurred. A saturated aqueous solution of this sub-oxyiodide gives, after filtration, a barely perceptible darkening on treatment with hydrogen sulfide, while a solution of silver nitrate produces a barely detectable opalescence. Sulfuric, acetic and hydrochloric acids, as well as sodium hydroxide, cause decomposition into metal and a more soluble trivalent bismuth salt. It is insoluble in alcohol and in an aqueous solution of potassium iodide. It reduces an acid solution of potassium permanganate.

As a further criterion of the chemical individuality of this subsalt, the conductivity of various samples was compared with that of the basic iodide,  $\text{BiOI}$ , formed as above from bismuth oxide, the method of procedure in determining the solubility being precisely as described in a previous paper.<sup>6</sup> The measured resistance of the oxyiodide was found to be by two tests  $745 \pm 15$  ohms; that of the sub-oxyiodide was  $9000 \pm 900$  ohms.

**The Red Volatile Product.**—Mention has been made of the fact that a red, volatile, crystalline product separated in the tubes leading from the oven. This occurred in all cases. In order to test whether this substance was produced during the distillation by a side reaction, or was the product of the decomposition of the sub-oxyiodide, a sample of the latter compound was sealed to the pump, evacuated, and heated to  $262^\circ$ . After prolonged evacuation no sign of such a volatile substance outside the oven could be detected.

During each distillation small quantities of these bright red crystals, rarely more than 0.04 g., were formed. In order to determine the percentage of bismuth which they contained, the crystals were weighed into a platinum crucible, covered with dil. nitric acid, evaporated to dryness and gently ignited. Control experiments performed with a similar weight of the trioxide of bismuth showed that the analysis by this method could

<sup>6</sup> *J. Chem. Soc.*, 111, 29 (1917).

be relied on to yield a result correct to 0.1 mg. The balance used was sensitive to 0.05 mg. The iodine was determined by treating the crystals with an aqueous solution of silver nitrate to which dil. nitric acid was afterwards added to dissolve out traces of metallic bismuth. The precipitate of silver iodide was gathered on a Gooch crucible, according to the ordinary procedure. Three analyses of bismuth were carried out and two of iodine showing 44.9, 44.8 and 45.0 (av. 44.9) % of bismuth, and 55.2 and 54.9 (av. 55.05) % of iodine, as compared with 45.04 % of bismuth and 54.96 % of iodine calculated. The results agree very closely with the percentage composition of  $\text{BiI}_2$ . Such a compound has been described by Bertholet,<sup>7</sup> who obtained it in the form of metallic, leafy crystals by melting together iodine and bismuth.<sup>8</sup> The following description throws doubt upon the chemical identity of the product obtained in these earlier experiments. The crystals of bismuth subiodide obtained by the distillation of methyl iodide over bismuth suboxide are of a bright red color, and form long needles in the orthorhombic system. On treatment with water freed from dissolved oxygen a solution was obtained which gave much stronger reactions for bismuth and iodine than given by the suboxyiodide. In the absence of oxygen the subiodide dissolves without decomposition in ethyl alcohol and in methyl iodide, forming in both cases a clear yellow liquid. It is also freely soluble in an aqueous solution of potassium iodide, producing a solution closely resembling in appearance that of potassium dichromate. Bismuth subiodide rapidly reduces an aqueous solution of iodine and an acid solution of permanganate. On heating above 400° it decomposes into bismuth tri-iodide which volatilizes, leaving a residue of bismuth.

**The Pale Yellow Product from the Distillate.**—The distillate of methyl iodide was yellow in color. On cooling this with liquid ammonia, a white, curdy precipitate separated, which redissolved immediately on warming to room temperature. In the absence of air this distillate remained yellow and homogeneous for 9 days at a temperature between 15° and 20°, but shortly after the admission of air or of oxygen, about 0.05 g. of a white solid separated in each experiment. In the course of a few days the color of this solid turned to a distinct yellow while the supernatant liquid lost its color. Analysis of this solid showed that in all cases bismuth, iodine and carbon were present, while its separation only in the presence of oxygen is sufficient confirmation of the presence of this element. Analyses of the bismuth and iodine content showed that the composition of the solid varies from experiment to experiment, the last two samples showing 90.3 and 85.2% of bismuth, and 5.8 and 9.4 % of iodine, respectively; and in some of the analyses the percentage of bismuth fell as low as 71% and

<sup>7</sup> Bertholet, Ref. 4.

<sup>8</sup> See also Weber, Ref. 4.

the iodine was as high as 22 %. The yellow product was insoluble in alcohol and proved to be a strong reducing agent, for its addition to an aqueous solution of silver nitrate caused the precipitation of a mixture of silver and silver iodide. The above facts appear to be best interpreted on the assumptions that, (1) the distillate contains a varying quantity of the volatile bismuth subiodide carried over in the vapor of methyl iodide; (2) there is also present in the distillate bismuth dimethyl ( $\text{Bi}(\text{CH}_3)_2$ ) for it is extremely improbable that a volatile compound could exist wherein the ratio of bismuth to iodine is as high as 90.3:5.8 or even 85.2:9.4.

The first of these hypotheses was tested by inserting a short fractionating column between the reaction vessel and the condenser. The result was to make a marked reduction in the amount of iodine present in the solid, while the color of the solid became nearly white. It was also shown that bismuth subiodide, dissolved in methyl iodide, does slowly oxidize in air (oxygen) with the production of a yellow powder.

Owing to the small amount of material available it was impossible to test the second hypothesis conclusively. The percentage composition rules out the possibility that the whole of the bismuth came over in combination with iodine, and the most reasonable supposition appears to be that it distilled over in the form of a methyl compound. Bismuth trimethyl is well known, but it has been shown by Marquardt<sup>9</sup> that the halogens do not oxidize this compound, but replace the methyl groups. Hence the oxidation of bismuth trimethyl by oxygen could not yield a product possessing reducing properties sufficient to account for the reduction of silver nitrate to metallic silver.

Since the author has shown that the oxidation product of bismuth subiodide, formed by the action of oxygen upon a solution of the subiodide in methyl iodide, does not possess such reducing power, the most tenable hypothesis is that bismuth is carried over in the distillate as bismuth dimethyl, which on oxidation passes into such a compound as dimethoxy bismuth,  $\text{Bi}(\text{OCH}_3)_2$ .

### Summary.

1. Bismuth sub-oxyiodide,  $2\text{BiI}_2 \cdot 3\text{BiO}$ , a brick-red powder of considerable stability, has been isolated.
2. Bismuth subiodide,  $\text{BiI}_2$ , has been prepared as a red, volatile crystalline substance, belonging to the orthorhombic system.
3. Evidence has been adduced that bismuth dimethyl,  $\text{Bi}(\text{CH}_3)_2$ , has been isolated. It oxidizes readily and produces a strongly reducing substance, possibly dimethoxy bismuth,  $\text{Bi}(\text{OCH}_3)_2$ .

BRISBANE, AUSTRALIA.

<sup>9</sup> Marquardt, *Ber.*, 20, 1517 (1887).

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, PRINCETON UNIVERSITY.]

## THE REDUCTION OF SOLUTIONS OF FERRIC SALTS WITH MERCURY.

By LEROY W. MCCAY AND WILLIAM T. ANDERSON, JR.

Received July 22, 1921.

### Historical.

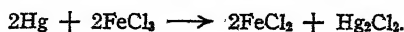
K. Schaffhäutl<sup>1</sup> seems to have first recognized the fact that mercury reduces aqueous solutions of ferric chloride, or more rapidly after the addition of hydrochloric acid, with the formation of ferrous chloride and mercurous chloride. The same observation was made many years later by Carnegie;<sup>2</sup> and in 1911 Borar<sup>3</sup> showed the reaction to be so complete that mercury can be used as a reducing agent for ferric compounds in the quantitative estimation of iron.

This method of reducing ferric chloride solutions was observed independently by one of us (M) over a year ago and supposed at the time to be new, for there is not even a reference to it either in the works of Rose and Fresenius, or in the most recent editions of the treatises on volumetric analysis by Classen<sup>4</sup> and by Beckurts.<sup>5</sup>

Our experience has been that the conclusion arrived at by Borar is correct. His description of the method, however, is unsatisfactorily brief, and since but two quantitative results are given to substantiate his claim, it seemed well to make a detailed study of the reaction, especially as regards its application to the preparation of ferrous chloride solutions prior to titrating them with potassium permanganate or dichromate.

### Theoretical.

When a solution of ferric chloride, containing or not containing free hydrochloric acid, is shaken violently for a few minutes in the presence of metallic mercury, the iron is completely reduced to the ferrous condition, an equivalent amount of mercurous chloride being formed.



The filtrate from the slate-colored mass of finely divided mercury and mercurous chloride gives upon the addition to it of potassium thiocyanate no red color. A solution of ferric sulfate, containing or not containing

<sup>1</sup> Schaffhäutl, *Ann.*, 44, 25 (1842).

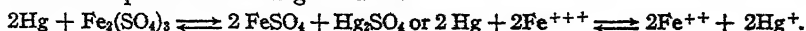
<sup>2</sup> Carnegie, *J. Chem. Soc.*, 53, 471 (1888).

<sup>3</sup> Borar, *ibid.*, 99, 1415 (1911).

<sup>4</sup> Classen, "Theorie u. Praxis der Massanalyse," Akademische Verlagsgesellschaft, Leipzig, 1912.

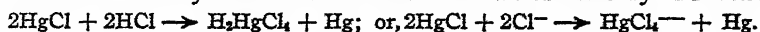
<sup>5</sup> Beckurts, "Die Methoden der Massanalyse," Vieweg u. Sohn, Braunschweig, 1913.

free sulfuric acid, is but partially reduced (at 20°) when similarly treated, a state of equilibrium being reached.



However, on adding a little hydrochloric acid and again shaking, a complete reduction to the ferrous state is effected. Indeed, a solution of ferric sulfate containing no free hydrochloric acid, but sodium or potassium chloride instead is also completely reduced when shaken violently in the presence of mercury. An amount of sodium chloride equivalent to the quantity of mercurous sulfate formed according to the above equation is sufficient for this purpose.

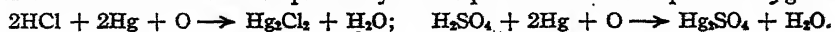
Although mercurous chloride is an exceedingly insoluble salt,<sup>6</sup> the liquid after reduction always contains a minute amount of mercury in solution.<sup>7</sup>



Its presence is indicated by the black precipitate which appears when a current of hydrogen sulfide is passed into the filtrate. The quantity is so small that thus far we have made no attempt to determine it quantitatively.

In reducing with mercury hydrochloric acid solutions of ferric chloride, containing or not containing sulfuric acid, no especial attention need be paid to the amounts of free acids present, providing of course their concentrations are kept within reasonable limits. If, however, as will be shown later, the Zimmermann-Reinhardt modification of the permanganate method be employed for titrating the ferrous chloride, the 100 to 150 cc. of the solution to be reduced should contain not over 10 cc. of hydrochloric acid, sp. gr. 1.18-1.19.

The exceedingly small amounts of mercurous chloride and sulfate formed when dil. hydrochloric and sulfuric acids are shaken with mercury for 4 or 5 minutes are due most probably to the presence of atmospheric oxygen.<sup>8</sup>



The reactions proceed slowly, but in the course of several days, or a week, the quantities of mercurous salts formed are relatively large. Their presence has, of course, no bearing on the reduction of the ferric solutions.

### Experimental.

The reductions were made in a long, narrow glass bottle of about 800 cc. capacity, provided with a well-ground neck, and tightly fitting well-ground glass stopper. On shaking such a bottle the mercury present is more readily broken up into tiny globules and the reduction of the ferric

<sup>6</sup> Fresenius, "Quantitative Analyse," Vieweg u. Sohn, Braunschweig, 1875, 1, p. 183.

<sup>7</sup> Ostwald, "Principles of Inorganic Chemistry," Macmillan and Co., New York, 1902, pp. 660, 669.

<sup>8</sup> Berthelot, *Ann. chim. phys.*, [5] 23, 100 (1881). See also Bailey, *J. Chem. Soc.*, 53, 760 (1888).

salt accelerated. About 20 cc. of redistilled mercury<sup>9</sup> (270 g.) was placed in the bottle, the ferric chloride solution (100 to 150 cc.) containing 10 cc. of hydrochloric acid, sp. gr. 1.18-1.19, added, the stopper introduced, and the whole shaken vigorously for from 4 to 5 minutes. We have found that when 0.1400-0.1800 g. of iron is present the reduction is always complete at the end of 5 minutes. The stopper was then removed, washed off into a beaker, the solution along with any suspended mercurous chloride decanted into the same beaker, and the liquid then filtered by suction. The mixture of mercury and mercurous chloride remaining in the bottle was washed by decantation 5 times, 20 cc. of water being employed for each washing. All separate wash waters were poured first into the beaker and then through the filter, the final volume of the liquid amounting to about 300 cc. Since the mercury in the bottle after a reduction, although mixed with mercurous chloride, is still as active as when first used, we simply stopper the bottle and place it aside so that it may be ready at any moment for further reductions. The mixture of mercurous chloride and finely divided mercury remaining in the beaker and on the filter paper may be preserved and, when a sufficient amount has collected, the mercury may be recovered by covering the mass with a strong solution of stannous chloride, adding hydrochloric acid, and heating for several hours.

In a number of solutions so reduced the iron was determined by the Zimmermann-Reinhardt,<sup>10</sup> as well as by the Penny<sup>10</sup> method.

1. The solution consisted of pure crystalline ferric ammonium sulfate, a liter at 20° containing 14.0765 g. of the salt and 100 cc. of hydrochloric acid, sp. gr. 1.18. The strength of the solution was unknown to the experimenter (A.). He used 100 cc. for each determination. Using the Zimmerman-Reinhardt method and 0.1 *N* potassium permanganate he obtained 0.1627, 0.1625, 0.1630, and 0.1627 g. of iron; with the Penny method and 0.1 *N* potassium dichromate he obtained 0.1624, 0.1627, 0.1629, 0.1631, 0.1627, and 0.1627 g. of iron. The average for the former method is 0.1627; for the latter, 0.1627 g. His results agree well with the amount which theory demands, 0.1630 g. The average time necessary to make a determination according to Zimmermann-Reinhardt was 21, according to Penny, 29 minutes. The difference, 8 minutes, is the time required to obtain the end-point on the porcelain spot plate. The average time for filtering and washing combined was 11 minutes. Different analysts require, of course, different intervals of time in which to perform the same operations, still the above will give a fair idea as to the amount of time involved in making a determination, after the substance containing the iron is once in solution.

2. A specimen of finely ground hematite was used. The percentage of iron present was unknown to the experimenter (A.). The ore was dissolved in conc. hydrochloric acid, water added and the small amount of insoluble matter removed by filtration.

The latter was fused with a little sodium carbonate, the melt dissolved in dil.

<sup>9</sup> G. A. Hulett, *Phys. Rev.*, 21, 6 (1905).

<sup>10</sup> Treadwell-Hall, "Quantitative Analysis," John Wiley and Sons, New York, 1915, pp. 609 and 641.

hydrochloric acid and the solution added to the main portion. The reduction was carried out as already described. By the Z.-R. method 62.92 and 62.90% of iron were found; by the Penny method 62.94 and 62.94%. The ore had been carefully examined by reducing its sulfuric acid solution with zinc in a Jones reductor, and titrating with potassium permanganate. By this method 62.85% (av.) of iron was found, as compared with 62.92% (av.) found by reduction with mercury in hydrochloric acid solution.

3. Magnetite (Sample 29) from the Bureau of Standards was used. The ore was first dried at 100° to constant weight, and then dissolved in conc. hydrochloric acid exactly as described under (2). In this case also the iron content was unknown to the experimenter (A.). The Z.-R. method gave 55.67, 55.68 and 55.71% of iron; and the Penny method, 55.72, 55.67, 55.64%; average 55.68%. According to the Bureau of Standards the ore contains 55.75% of iron.<sup>11</sup>

Since titanous acid is *not* reduced by mercury the method may be employed in determining iron in titaniferous ores and minerals. That the presence of titanous acid in the solution introduces no error will be evident from the following results.

TABLE I.  
DETERMINATION OF IRON IN THE PRESENCE OF TITANIC ACID.

Fe taken, <sup>a</sup> G.	TiO <sub>2</sub> taken. G.	Fe found. G.
0.1416	0.0903	0.1413
0.1879	0.0087	0.1880
0.1879	0.0113	0.1877
0.1517	0.0158	0.1517

<sup>a</sup> Calculated from amount of crystallized ferric ammonium sulfate weighed out in each case.

The titrations were carried out according to the Z.-R. method.

To get some idea as to the amount of ferric iron reduced by mercury when the solution is a sulfuric acid one, we prepared 500 cc. of a solution containing 8.1161 g. of crystalline ferric ammonium sulfate and 25 cc. of conc. sulfuric acid. This was poured into a dry bottle containing 20 cc. of pure mercury, the bottle was stoppered, shaken violently for 10 minutes, and the whole let stand for 30 minutes. The entire operation was carried out at 20°. Since the supernatant liquid was now perfectly clear, 50 cc. was pipetted into a beaker, the mercurous mercury in solution was precipitated with dil. hydrochloric acid as mercurous chloride, this filtered off, and the filtrate titrated with permanganate according to the Z.-R. method. The removal of the mercurous mercury is imperative, for solutions of mercurous salts reduce permanganate. The bottle and contents were shaken again at intervals, and after one hour, 50 cc. was removed and treated as before. The procedure was repeated, the intervals being lengthened each time.

<sup>11</sup> Dr. Shimer of Easton, Pa., found 55.65 % Fe.

TABLE II.  
FERRIC IRON REDUCED BY MERCURY.  
(No chlorides present.)

Expt.	50 cc. of solution = 0.0939 g. of Fe.		
	Elapsed time. Hours.	Fe(ous) found. G.	Fe reduced at 20°. %.
1	0.5	0.0499	53.22
2	1.5	0.0498	53.08
3	4	0.0499	53.22
4	30	0.0499	53.22
5	148	0.0497	52.95
6	444	0.0499	53.22
		Av.	53.15%

In the circumstances, then, the state of equilibrium was reached when somewhat over half the iron had been reduced to the ferrous condition.

When a solution of ferrous sulfate containing free sulfuric acid is shaken with mercurous sulfate and mercury a part of the ferrous salt is oxidized to the ferric salt, the following reaction taking place.



This reaction is, of course, the reverse of the above, but the time required to reach the equilibrium position is in this case considerable. Thus far we have made no attempt to determine the extent of oxidation in any specific case.

That the presence of a very small amount of sodium chloride in a solution of ferric sulfate (even when no free sulfuric acid is present) is sufficient to further a complete reduction of the iron to the ferrous condition when the solution is shaken with mercury will be evident from the following experiment.

0.5002 g. of ferrous ammonium sulfate (= 0.0712 g. of Fe) and 0.5985 g. of crystallized ferric ammonium alum (= 0.0692 g. of Fe) were dissolved in about 100 cc. water, exactly 0.0725 g. of sodium chloride (amount equivalent to the mercury oxidized) was added, the solution reduced with mercury, the mercurous chloride filtered off, the filtrate acidified strongly with sulfuric acid, diluted to 250 cc., and the iron determined with 0.1 *N* potassium dichromate solution. The iron found was 0.1405 g. compared with 0.1404 g. present.

As we have already pointed out, the reaction which takes place when a solution of ferric sulfate is shaken in the presence of mercury may be represented by  $2\text{Hg} + \text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{FeSO}_4 + \text{Hg}_2\text{SO}_4$ . Since 56 g. of iron is, according to the above equation, equivalent to 200 g. of mercurous mercury, 28 g. of iron is equivalent to 100 g. of mercury which in turn is equivalent to 29.25 g. of sodium chloride. Fifty cc. of 0.1 *N* potassium permanganate shows the presence of 0.28 g. of pure iron, and 0.3 g. sodium chloride is a little more than necessary to precipitate the mercury in the mercurous sulfate formed during the complete reduction of the 0.28 g. of iron to the ferrous state. If then we add to a sulfuric acid solution of ferric sulfate, containing not more than 0.28 g. of iron, 0.3 g. of sodium chloride dissolved in a little water, and shake the solution with mercury, we can, after filtering off the mercurous chloride, dilute the filtrate to 500 cc. and *without* adding the Z.-R. mixture proceed at once to titrate with the per-



manganate. The end-point is sharp, the pink color persisting for at least 5 minutes. The results are very satisfactory as will be evident from those given below.

A solution of crystallized ferric ammonium alum was prepared containing in 250 cc. 12.1813 g. of the salt and 5 cc. of conc. sulfuric acid. For each determination 25 cc. (=0.1410 g. of Fe) was taken, 0.3 g. of sodium chloride added, the solution diluted to 100 cc. and the reduction effected with mercury. The filtrate from the mercurous chloride was mixed with more sulfuric acid, diluted to 50° cc. and titrated at once with permanganate solution. 25 cc. = 0.1410 g. Fe. Our analyses showed 0.1411, 0.1414, 0.1408 and 0.1412 g. of iron, (av. 0.1411 g.) as compared with 0.1410 taken.

This method for reducing with mercury solutions of ferric salts is quick, accurate and very convenient. Barring the ordinary reagents and apparatus which are always at hand, only a well stoppered bottle and pure mercury are necessary. The mixture of mercury and mercurous chloride remaining in the bottle may be used over and over again, for after 33 reductions we have found it to be fully as active as was the original pure mercury.

In view of this, as well as of the fact that while zinc reduces titanous acid and mercury does not, the latter metal has an advantage over the former in preparing iron compounds for titration. Moreover, the zinc in a Jones reductor oxidizes rapidly, unless the metal be kept covered with water, and time is required to dissolve out the products of the oxidation with sulfuric acid so that the zinc will function properly. In using stannous chloride a number of details must be carefully observed, and solutions of the salt deteriorate rapidly unless preserved in a non-oxidizing atmosphere. Solutions of ferric salts, containing titanous acid, are frequently reduced at their boiling points with hydrogen sulfide or sulfur dioxide. The procedure is tedious, for to expel the excess of gas continued boiling with subsequent cooling in a current of an indifferent gas is necessary. It is evident also that if the indifferent gas contain traces of air, small amounts of ferrous salt may be reoxidized during the cooling of the solution.

Solutions of potassium ferricyanide, potassium chromate, ammonium molybdate, sodium vanadate, potassium antimoniate, etc., when acidified with hydrochloric acid and shaken with mercury are reduced. Some of these reactions are being investigated.

### Summary.

1. Solutions of ferric chloride, containing or not containing free acid, are rapidly and completely reduced when shaken in the presence of mercury. The same is true of solutions of ferric sulfate, providing a little free hydrochloric acid or alkali chloride be present. Under similar conditions titanous acid is not reduced.

2. A number of determinations of the iron in crystallized ferric ammonium alum, in hematite and in a specimen of magnetite from the Bureau

of Standards prove that this method of reduction is quick, accurate and most convenient.

3. Some of the advantages of the method over those most commonly employed have been outlined.

4. Mention is made of a number of other substances whose solutions are reduced by mercury.

PRINCETON, NEW JERSEY.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

## THE SEPARATION OF COLUMBIUM AND TANTALUM BY MEANS OF SELENIUM OXYCHLORIDE.<sup>1</sup>

By HENRY BALDWIN MERRILL.

Received July 22, 1921.

It was found by Lenher<sup>2</sup> that columbium oxide is soluble in a mixture of sulfuric acid and selenium oxychloride, while tantalum oxide is insoluble, or very much less soluble, in the same reagent. This appeared to afford a means of separating the two elements. The purpose of the present investigation was to work out the best experimental conditions for accomplishing the separation.

**Previous Methods.**—The separation of columbium and tantalum has hitherto been one of the most difficult tasks with which the chemist is confronted. In their chemical properties, the corresponding compounds of the two elements show hardly any points of divergence which are sharp enough to be used for methods of separation. Of the various methods which have been proposed, only one—the double fluoride method of Marignac<sup>3</sup>—merits any consideration. The Marignac method consists of the crystallization of the normal potassium fluotantalate,  $K_2TaF_7$ , under such conditions of acidity and concentration of potassium fluoride that the columbium will form the more soluble oxyfluoride,  $K_2CbOF_5$ . The chief advantage of the Marignac method is that the two double fluorides are not isomorphous, and hence no mixed crystals should be obtained. The difference in crystal form affords a convenient means of following the course of the separation. The disadvantages of the method are many and serious. The ratio of the solubility of the columbium compound to that of the tantalum is only about 10 to 1, potassium columbium oxyfluoride being soluble in 12 parts of hot water, and potassium fluotantalate requiring about 120 parts. This necessitates many recrystallizations before an approximately complete separation is accomplished, and in no case can all of either constituent be obtained in a state of purity, since some of each will inevitably remain in the various mother liquors. From the analytical standpoint, this means that the Marignac method cannot be made other than a very rough one. Its limit of error is probably at least 10%. In addition to this inherent error, the method is liable to grave inaccuracies, due to the difficulty in maintaining the concentration of hydro-

<sup>1</sup> Abstract of a portion of a thesis presented to the University of Wisconsin, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1921. The work was financed in part by a grant from the University research fund.

<sup>2</sup> Lenher, *THIS JOURNAL*, 43, 29 (1921).

<sup>3</sup> Marignac, *Ann. chim. phys.*, [4] 3, 5, 49, 68 (1866). Simpson, *Chem. News*, 99, 243 (1909).

fluoric acid and of potassium fluoride constant within very narrow specified limits. If the acidity is too great, the columbium forms a normal fluoride; if too low, the tantalum may form an oxyfluoride; in either case, the whole basis of the separation is destroyed. If too much or too little potassium fluoride is present, double fluorides are formed in which the ratio of potassium fluoride to columbium or tantalum pentafluoride is more or less than 2 : 1. Finally, the Marignac method is extremely laborious and time-consuming, and requires the use of platinum vessels throughout.

**The Problem.**—In the ordinary course of analysis, columbium, tantalum and titanium are separated from the other elements as oxides. Titanium accompanies columbium in the Marignac separation, and no separation of columbium and titanium is known. Titanium dioxide and columbium pentoxide ( $\text{Cb}_2\text{O}_5$ ) are both soluble in selenium oxychloride and sulfuric acid. The problem, therefore, is to extract these two oxides completely from a mixture with tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ), under such conditions that the minimum amount of the last is dissolved. To ascertain these conditions, the effect of various factors upon the solubility of each oxide was first determined separately. From the data thus obtained, a tentative method of separation was formulated, and tested upon synthetic mixtures of the oxides.

**Reagents.**—The columbium and tantalum oxides employed were obtained from various commercial sources, and from stocks previously prepared in this laboratory. These oxides were further purified by the Marignac method.

Selenium oxychloride was prepared by the interaction of selenium dioxide and tetrachloride and was purified by vacuum distillation.<sup>4</sup> The purity of the other reagents employed was ascertained by the usual tests.

### Manipulation.

To determine the effect of various factors upon the solubility of each oxide, the oxide in question was boiled with the solution of selenium oxychloride and sulfuric acid in an Erlenmeyer flask, using a sand-bath. The mouth of the flask was covered with a small watch glass, the upper part of the flask acting as an air condenser, so that with proper regulation of the heat very little of the solvent was lost, and little or no hydrolysis of the oxychloride took place. The solution was filtered with suction, through an asbestos mat, in a Gooch crucible. In some cases, an excess of the oxide was employed, and the amount dissolved was determined in a known amount of the filtrate. In most instances a weighed sample of the oxide was employed, and the undissolved portion was transferred to the crucible, ignited, and weighed.

By this procedure, the effect of the following factors upon the solubility was determined: (1) composition of the reagent; (2) condition of the oxide, *i. e.*, hydration; (3) size of sample; (4) time of digestion; (5) amount of solvent employed. The temperature was in all cases the boiling point of the solvent.

<sup>4</sup> Lenher, *THIS JOURNAL*, 42, 2498 (1920).

The rate of solution of both oxides is slow, so that results obtained do not represent the true solubility, but rather the amount dissolved under definite experimental conditions in a short time (minutes or hours).

**Composition of the Reagent.**—Neither columbium oxide nor tantalum oxide is acted upon by selenium oxychloride alone. Columbium oxide is readily soluble in conc. sulfuric acid, even when the oxide is ignited. Tantalum oxide is soluble in sulfuric acid to a much less extent. The effect of adding selenium oxychloride to sulfuric acid is to decrease the solubility of both oxides. Experiments have shown that a mixture of equal parts by volume of the reagent constituents is best suited for the separation of columbium and tantalum pentoxides. When an excess of the oxide is boiled for 30 minutes with 50 cc. of this reagent, the approximate amounts of pentoxides dissolved are 0.35 g. and 0.005 g., respectively. In conc. sulfuric acid, the amounts dissolved are 0.9 g. and 0.08 g. The effect of increasing the ratio of the oxychloride to the acid beyond 1 : 1 is to decrease the solubility of columbium pentoxide much more than that of tantalum pentoxide.

Free sulfur trioxide as contrasted with sulfuric acid, has practically no solvent action upon either oxide. Solutions of fuming sulfuric acid in selenium oxychloride, such as were employed in Lenher's experiments, have about the same action as solutions of conc. sulfuric acid.

It is probable that the sulfuric acid attacks the oxide in the first instance, forming a loose addition compound which is soluble in selenium oxychloride. This is evidenced by the fact that, once the oxide has been dissolved, the solution may be diluted with selenium oxychloride to any extent without the formation of a precipitate.

**Hydration of the Oxides.**—The freshly precipitated hydrated oxides are much more readily soluble than are the ignited oxides. While the solubility decreases with increasing temperature of ignition, the solubility of hydrated tantalum peroxide is too great to permit the separation to be applied to the hydrated oxides, and good results can be obtained only when the oxides have been ignited at bright red heat.

**Effects of Size of Sample, Amount of Solvent and Time of Digestion.**—The effects of these factors are not the same upon the solubilities of both oxides. Tantalum pentoxide is so slowly soluble that equilibrium is not even approached in actual practice. Hence the amount dissolved is independent of the amount of solvent employed, and is directly proportional to the amount of solid oxide present, *i. e.*, to the surface exposed, and to the time of contact between solvent and solid. With columbium pentoxide, the process of solution is fairly rapid, so long as the amount of surface exposed is large. If the oxide is present in large excess, the amount dissolved is approximately proportional to the amount of solvent, and is independent of the amount of oxide taken and of the time, showing that equilibrium is at least approached. When, however, the amount of solid

columbium pentoxide is small, the rate of solution is very slow. If a large sample is treated with an excess of the reagent, the larger portion of the oxide is quickly dissolved, but the rate of solution becomes slower and slower as the area of contact between the phases diminishes. The solution of the last traces of columbium pentoxide takes place very slowly indeed. This means that *complete* solution of a given sample requires a considerable period of digestion, and furthermore that this period will be about the same whether the actual quantity of oxide originally taken is large or small.

Experiments have shown that an hour's boiling with the 1:1 reagent is required for the complete solution of a given sample of columbium pentoxide. So long as the solvent is present in excess, increasing the amount of solvent has little influence upon the time. Fifty cc. of solvent per 0.25 g. of columbium pentoxide has been found sufficient. The amount of tantalum pentoxide dissolved in this amount of reagent in an hour depends entirely upon the amount of this oxide which is present. It is obvious that from the analytical standpoint, the direction and magnitude of the errors are dependent upon the relative proportions of the two oxides which are present in a mixture. In all cases, there is some danger that traces of columbium pentoxide will not be dissolved. If the percentage of tantalum is low, very little tantalum pentoxide will be dissolved, and hence the results found will tend to be high for tantalum and low for columbium. If the percentage of tantalum is high, considerable amounts of tantalum pentoxide may be dissolved, in which case the results found will be low for tantalum and high for columbium. When the two oxides are present in approximately equal amounts, the two errors will be roughly compensatory.

The size of the sample employed must be kept as small as is consistent with percentage accuracy of weighing, in order to keep the amount of tantalum oxide present as small as possible. Samples of from 0.2 to 0.3 g. have been found to give the best results.

#### **Procedure for the Analysis of Mixed Oxides of Columbium and Tantalum.**

In accordance with the results of the experiments described above, the following method for the analytical separation of the two oxides is suggested.

1. The oxides are separated, together with titanium dioxide if the latter is present, from the other elements by the usual methods and the total percentage of tantalum and columbium pentoxides (plus titanium dioxide) is determined.

2. A weighed sample (0.2 to 0.3 g.) of the ignited oxides is boiled with 50 cc. of a 1:1 mixture of selenium oxychloride and conc. sulfuric acid in an Erlenmeyer flask on a sand-bath for half an hour, care being taken

that the boiling is not so vigorous that clouds of vapor are given off. The contents of the flask, after cooling, are decanted with suction through a weighed Gooch crucible. The filtrate is poured into a large volume of water, and the resulting solution is brought to a boil. A voluminous white precipitate of hydrated columbium pentoxide indicates the presence of columbium in the mixture. The residue in the flask is boiled with 20 cc. of the reagent for 15 minutes, the solution decanted through the crucible, and the filtrate poured into water. This process is repeated until the filtrate, upon hydrolysis, gives only a faint precipitate, due to traces of dissolved tantalum pentoxide. Care should be taken that as little as possible of the solid oxide is carried onto the filter in the first decantations, since this portion escapes treatment in the subsequent extractions. By this procedure, the course of the solution of the columbium oxide can be followed. Three or four treatments of the oxide with the reagent are usually enough to remove all the columbium pentoxide.

3. The undissolved tantalum pentoxide is transferred to the crucible with the jet from a wash-bottle. Complete washing of the oxide is not necessary, since all the decomposition products of the reagent are volatile. The crucible is ignited and weighed, the gain in weight representing the pentoxide. Columbium (plus titanium) is determined by difference. The titanium is best determined colorimetrically in a separate sample, and deducted from the columbium.

The method outlined above was applied to synthetic mixtures of tantalum and columbium pentoxides. In a number of experiments, the mixed oxides were fused with potassium hydrogen sulfate, and precipitated by hydrolysis, in order to simulate actual working conditions. The results obtained with these intimate mixtures were no different from those obtained with mechanical mixtures.

TABLE I.

SEPARATION OF MIXTURES OF TANTALUM AND COLUMBIUM PENTOXIDES.

	Expt.	1.	2.	3.	4.	5.	6.	7.
$Ta_2O_5$	taken.....	0.2151	0.1449	0.2040	0.1414	0.0411	0.0552	0.0178
	found.....	0.2130	0.1437	0.2019	0.1431	0.0477	0.0704	0.0304
$Cb_2O_5$	taken.....	0.0162	0.0525	0.1052	0.1043	0.1998	0.4875	0.4267
	found.....	0.0183	0.0537	0.1073	0.1026	0.1932	0.4723	0.4141

The maximum divergence of the results found from the amount taken is about 3% of the total amount taken, and is in the most cases much less. The errors are far smaller than those to which the Marignac method is liable. In simplicity and speed, the superiority of the separation proposed over the Marignac method is very marked. An analysis of the mixed oxides may be begun and completed in a few hours, using the

selenium oxychloride-sulfuric acid method, while days or even weeks are required by the Marignac method.

It is believed, therefore, that the method proposed for the separation of columbium and tantalum is superior to any other yet proposed.

### Procedure for the Preparation of Pure Oxides.

To prepare pure columbium pentoxide, the mixed oxides should be extracted with sufficient solvent to dissolve all of the columbium. The boiling should not be prolonged until all of the columbium is dissolved, since the object is to dissolve as little tantalum pentoxide as possible. The dissolved oxide is precipitated with water and ammonia, filtered, and ignited. Some tantalum pentoxide will inevitably be dissolved during the extraction, but by repeating the treatment upon the oxide obtained by the first extraction, very pure columbium pentoxide may be obtained, since the amount of tantalum pentoxide present during the second purification is so small that virtually no tantalum will be dissolved.

To prepare pure tantalum pentoxide, it is only necessary to extract the oxide with the reagent until all of the columbium is dissolved, sacrificing the portion of the tantalum which goes into solution. The complete removal of the columbium may be expedited by increasing the proportion of sulfuric acid in the reagent.

### Summary.

A method for the separation of columbium and tantalum, both for purposes of analysis and of purification, by means of selenium oxychloride and sulfuric acid, has been described.

This work was performed by the author while acting as research assistant to Professor Victor Lenher.

MADISON, WISCONSIN.

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## [CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.] THE SEPARATION OF MOLYBDENUM AND TUNGSTEN BY MEANS OF SELENIUM OXYCHLORIDE.<sup>1</sup>

BY HENRY BALDWIN MERRILL.

Received July 22, 1921.

It was found by Lenher<sup>2</sup> that molybdenum trioxide is soluble in selenium oxychloride, while tungstic oxide is insoluble in this reagent. Since none of the methods hitherto known for the separation of molybdenum and tungsten is entirely satisfactory, it was felt that this observation of Lenher's which appeared to afford a new method of separation, should be studied further. The purpose of the present investigation was to determine

<sup>1</sup> Abstract of a portion of a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the University of Wisconsin, 1921. This work was financed in part by a grant from the University research fund.

<sup>2</sup> Lenher, *THIS JOURNAL*, 43, 29 (1921).

whether, and with what degree of accuracy, molybdenum trioxide and tungsten trioxide can be separated by means of selenium oxychloride, and to determine the best conditions for the separation.

**Basis of the Separation.**—The solubility of molybdenum trioxide in selenium oxychloride varies with the physical state of the oxide. The freshly precipitated hydrated oxide is readily soluble; the ignited oxide, on the other hand, is soluble only with difficulty, so that complete solution of a given sample cannot be effected in days or weeks. However, the addition of small amounts of sulfuric acid to the selenium oxychloride causes the ignited molybdenum trioxide to dissolve with ease. Hydrated tungsten trioxide, as is well known, is peptized readily by many substances, and as it happens to be peptized by selenium oxychloride, it passes into the colloidal condition. Ignited tungsten trioxide is neither dissolved nor peptized by selenium oxychloride with or without the addition of sulfuric acid. The basis of the separation, is therefore, the extraction of molybdenum trioxide with selenium oxychloride and sulfuric acid from a mixture of ignited molybdenum and tungsten trioxides.

**Method of Attack.**—To determine the best conditions for the separation, preliminary experiments were first conducted with each oxide separately. Weighed samples of molybdenum trioxide were boiled with the reagent in small Erlenmeyer flasks, the mouths of the flasks being covered with small watch glasses to prevent hydrolysis of the selenium oxychloride by the moisture of the air. One g. samples were employed, and the digestion was continued until solution was complete, or until no further action could be detected. The factors varied were the ratio of sulfuric acid to selenium oxychloride, and the volume of the solvent. Control experiments were conducted with tungsten trioxide, 1g. samples being digested with the reagent, the solution filtered through weighed Gooch crucibles with asbestos mats and the undissolved oxide transferred to the crucibles, ignited, and weighed. The amounts dissolved were thus determined by difference.

**Reagents.**—The oxides of molybdenum and tungsten were prepared by ignition of their ammonium salts which had been purified by repeated recrystallizations. Selenium oxychloride was prepared by the interaction of selenium dioxide and selenium tetrachloride,\* the product being distilled in a vacuum. The purity of the other reagents employed was ascertained by the customary tests.

#### Behavior of the Pure Oxides.

Preliminary experiments seemed to show that ignited tungsten trioxide was slightly soluble in selenium oxychloride and sulfuric acid. The losses, when 1g. samples were treated with 30 cc. of the solvent, amounted to several milligrams and their magnitude appeared to be independent of the composition or the volume of the reagent, and of the time of di-

\* Lenher, *THIS JOURNAL*, 42, 2498 (1920).



gestion. Examination of the selenium oxychloride filtrate and of the wash-water employed in transferring the undissolved oxide from the flask to the crucible showed that all of the dissolved oxide was contained in the latter. The losses were therefore due to peptization of the tungsten trioxide by the wash-water. It was found to be impractical to transfer the oxide to the crucible with a jet of selenium oxychloride, due to the rather high viscosity of the latter. Various solutions of electrolytes were employed for this purpose, and good results were obtained with a hot, 10% solution of ammonium nitrate. When this solution was employed the amount of tungsten trioxide dissolved was only a few tenths of a mg.

The experiments with tungsten trioxide having shown that this oxide is insoluble under all conditions in selenium oxychloride and sulfuric acid, the conditions for the separation could be adjusted solely with reference to dissolving the molybdenum trioxide. It was found that both the amount of solvent and the time required to effect the complete solution of a given sample of molybdenum trioxide decreased with increasing concentration of sulfuric acid in the reagent. Thus the time required to dissolve 1 g. of molybdenum trioxide in 30 cc. of solution containing 15 cc., 5 cc., and 2 cc. of sulfuric acid, was 30 minutes, 45 minutes, and 60 minutes, respectively. When the reagent contained less than 2 cc. of sulfuric acid per 30 cc. of solution, complete solution of 1 g. of oxide in 30 cc. of solvent could not be effected. It was found desirable to keep the sulfuric acid concentration low, as the viscosity of the reagent increases with increasing concentration of the acid. The reagent which was found to be most satisfactory, taking all factors into consideration, was a mixture of 1 part of sulfuric acid and 5 parts of selenium oxychloride. Thirty cc. of this reagent will dissolve 1 g. of molybdenum trioxide in 45 minutes at the boiling point of the solvent.

### Separation of Mechanical Mixtures.

The separation of mechanical mixtures of molybdenum and tungsten trioxides was next attempted. One-g. samples of known composition were boiled with 30 cc. of the reagent for an hour, the solution decanted through weighed Gooch crucibles, the residues washed several times with small portions of selenium oxychloride, and finally brought on the filter with hot, 10% ammonium nitrate solution. The crucible was ignited and weighed, the gain in weight representing tungsten trioxide. Molybdenum trioxide was determined by difference. The results of a few of these experiments, chosen at random from the large number of separations performed, are given in Table I.

It will be seen that the errors are in all cases small, which shows that the separation for molybdenum and tungsten with this reagent is a *very* accurate one.

TABLE I.  
SEPARATION OF MECHANICAL MIXTURES OF MOLYBDENUM AND TUNGSTEN  
TRIOXIDES.

Expt.	1.	2.	3.	4.	5.	6.	7.	8.
WO <sub>3</sub> taken.....	0.0034	0.3330	0.2071	0.3506	1.4238	0.7500	0.7333	0.5065
WO <sub>3</sub> found.....	0.0032	0.3337	0.2074	0.3501	1.4224	0.7449	0.7327	0.5068
MoO <sub>3</sub> taken.....	0.4967	1.5443	0.7437	0.7594	0.9435	0.2500	0.0856	none.
MoO <sub>3</sub> found.....	0.4969	1.5436	0.7434	0.7599	0.9449	0.2501	0.0862	none.

### Separation of Intimate "Chemical" Mixtures.

The mixtures which were separated in the above experiments are not strictly comparable to those which are met with in actual practice. The samples which were separated in the experiments reported in Table I were simply mechanical mixtures of the ignited, finely ground oxides, while in actual practice the oxides would be obtained in a much more intimate state of admixture. Mixtures of tungsten and molybdenum trioxides are usually obtained by the ignition of their mercurous salts, precipitated together; by ignition of their ammonium salts, crystallized together; or by the decomposition of a mineral with aqua regia. When the separation of such mixtures (which may be called "chemical") prepared by dissolving known amounts of the oxides in ammonia, evaporating to dryness and igniting to oxide, was attempted, it was found that the separation proposed is of somewhat limited applicability. When the mixture contains more than about 10% of tungsten trioxide, complete extraction of the molybdenum cannot be effected, no matter how long the digestion is continued, or how much sulfuric acid is added to the selenium oxychloride. The molybdenum and tungsten trioxides apparently form a solid solution, the tungsten trioxide preventing the solution of the molybdenum trioxide unless the latter is present in large excess. When less than 10% of tungsten trioxide is present, the molybdic oxide can be completely extracted. In this case, however, the small amount of tungsten trioxide which was dispersed through the predominant molybdenum trioxide is left in a very fine state of division, and tends to run through the filter, causing serious losses. This difficulty was overcome by dissolving the mixed oxides in ammonia, and adding enough nitric acid to precipitate most of the tungsten, which thus had a chance to segregate from the molybdenum trioxide. The solution was then evaporated to dryness, and the residue ignited at dull red heat. Weighed samples of the mixed oxides so prepared were separated with selenium oxychloride and sulfuric acid as previously described. The results of these experiments are given in Table II.

TABLE II.  
SEPARATION OF CHEMICAL MIXTURES OF MOLYBDENUM AND TUNGSTEN  
TRIOXIDES.

Expt.	1.	2.	3.	4.
WO <sub>3</sub> taken.....	0.0717	0.0417	0.0223	0.0156
WO <sub>3</sub> found.....	0.0720	0.0409	0.0243	0.0163
MoO <sub>3</sub> taken.....	0.6177	0.7439	0.7264	0.8570
MoO <sub>3</sub> found.....	0.6174	0.7447	0.7254	0.8563

These experiments show that the separation of these two oxides is possible by means of selenium oxychloride and sulfuric acid.

### Summary.

A new method has been described for the separation of molybdenum and tungsten, consisting in the extraction of molybdenum trioxide from a mixture of the ignited oxides by means of selenium oxychloride.

This work was performed by the writer while acting as research assistant to Professor Victor Lenher, whom the writer takes this occasion to thank for all his help and kindness.

MADISON, WISCONSIN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE.]

## THE SPEED OF REACTION IN CONCENTRATED SOLUTIONS AND THE MECHANISM OF THE INVERSION OF SUCROSE.

BY GEORGE SCATCHARD.

Received July 27, 1921.

### Introduction.

Although the speed of inversion of sucrose in acid solutions has been studied more than the kinetics of any other reaction,<sup>1</sup> there are two anomalies which were discovered by the earliest workers, but which have not yet received an adequate explanation. According to the accepted theories of chemical kinetics, the speed of reaction ought to be independent of the concentration of sucrose and proportional to the concentration of the hydrogen ion. Experimentally, the speed increases more rapidly than the concentration of the hydrogen ion when that of the sugar is kept constant; and when the concentration of acid is unchanged the speed increases rapidly with increasing sugar concentration.

There have been three types of explanation of these anomalies offered. The one most generally accepted at the present time explains only the abnormal increase with increased acid concentration or on the addition of a salt. This theory assumes that the non-ionized acid exerts a catalytic effect, which may be even greater than that of the hydrogen ion itself.<sup>2</sup> However, this theory alone is not sufficient as is shown by the facts that it will not explain the change in speed with changing sugar concentration, and that different values are calculated for the activity of the non-ionized

<sup>1</sup> A good bibliography up to 1906 is given by R. J. Caldwell, *Brit. Assoc. Rep.*, (York), 1906, pp. 267-92.

<sup>2</sup> The following references are typical of a voluminous literature in this field.

H. C. S. Snelthage, *Z. Elektrochem.*, 18, 539 (1912); *Z. physik. Chem.*, 85, 211 (1913).

S. F. Acree, *Am. Chem. J.*, 49, 345 (1913).

H. S. Taylor, *Medd. K. Vetenskapsakad. Nobelinst.*, 1913; *Z. Elektrochem.*, 20, 201 (1914).

acid from the effect of increasing acid concentration and from the effect of the addition of a salt with a common anion.<sup>3</sup>

A second method of explaining these anomalies is based on the assumption that the speed of reaction in solutions is not strictly proportional to the concentrations in moles per liter of the reactants. Wilhelmy,<sup>4</sup> the pioneer in this field, empirically divided the weight of acid by that of water and found the resulting speed much more nearly constant. Spohr<sup>5</sup> considered the effect due to the displacement of water by sugar, and he found that the speed of reaction was independent of the sugar concentration if the ratio of water to acid was kept constant. This method is equivalent to the use of the weight-normal concentrations of Morse,<sup>6</sup> and it has been much used by Armstrong and his co-workers.<sup>7</sup> Cohen<sup>8</sup> accomplishes practically the same result by making a correction for the volume occupied by the sugar, similar to the "b" term in van der Waals' equation. All these methods neglect the fact that the water takes part in the reaction.

The third type of explanation is that of Arrhenius<sup>9</sup> that the speed of reaction in solutions is proportional, not to the concentrations of the reactants, but to their osmotic pressures. The difficulty of this idea is the ambiguity of the osmotic pressure of a single component of a solution. At times the osmotic pressure seems to be identical with the activity as defined by G. N. Lewis,<sup>10</sup> and for such cases the theory of Arrhenius is identical with that which will be presented in this paper.

A great step in advance was made when Jones and Lewis<sup>11</sup> measured the activity of the hydrogen ion by means of the hydrogen electrode. Assuming that the speed of reaction is proportional to this activity of the hydrogen ion rather than to its concentration, they find it also proportional to the concentration of water in moles per liter, and they draw the conclusion that the reaction proceeds by the combination of a molecule of sugar with a hydrogen ion, and that this complex ion reacts with one molecule of water to form glucose and fructose and to re-form the hydrogen ion. The present paper is an extension of the substitution of activity for

<sup>3</sup> For example see H. S. Taylor and H. W. Close, *THIS JOURNAL*, 39, 422 (1917).

<sup>4</sup> L. Wilhelmy, *Pogg. Ann.*, 81, 499 (1850).

<sup>5</sup> J. Spohr, *J. prakt. Chem.*, [2] 33, 265 (1886).

<sup>6</sup> H. N. Morse, *Carnegie Inst. Pub.*, 198, 97 (1914).

<sup>7</sup> H. E. Armstrong and others, "Studies of the Processes Operative in Solutions," in the *Proc. Roy. Soc. (London)*, *J. Chem. Soc. and Chem. News*, 1906-13.

Especially R. J. Caldwell, *Proc. Roy. Soc.*, 78A, 272 (1906), and F. P. Worley, *J. Chem. Soc.*, 99, 349 (1911).

<sup>8</sup> E. Cohen, *Z. physik. Chem.*, 23, 442 (1897).

<sup>9</sup> S. Arrhenius, *Z. physik. Chem.*, 28, 317-35 (1899).

<sup>10</sup> S. Arrhenius and E. Andersson, *Medd. K. Vetenskapsakad. Nobelinst.*, 3, No. 25 (1917).

<sup>11</sup> G. N. Lewis, *Proc. Am. Acad.*, 37, 49 (1901); *THIS JOURNAL*, 35, 16 (1913).

<sup>12</sup> C. M. Jones and W. C. McC. Lewis, *J. Chem. Soc.*, 117, 1120 (1920).

concentration to the other reactants as well as to the hydrogen ion. The conclusions as to the mechanism of the reaction are very different from those of Jones and Lewis.

### The Formula for the Speed of Reaction in Solutions.

The formula for the speed of reaction in perfect gas systems is derived very simply from the kinetic theory: the speed is proportional to the concentration of each reacting species raised to the power which represents the number of molecules of that species which enter into the reaction according to the chemical equation. Given the reaction



the speed of reaction would be given by

$$s = dx/dt = K(C_1 - n_1'x)^{n_1}(C_2 - n_2'x)^{n_2}(C_3 - n_3'x)^{n_3} \quad (1)$$

where  $A_1$ , etc., represent the chemical formulas of the substances;  $n_1$ , etc., represent the number of molecules reacting; and  $n_1'$ , etc., represent the number of molecules which disappear when  $n$  molecules react.  $n_1'$  will be less than  $n_1$  when the substance  $A_1$  acts catalytically; it will be greater than  $n_1$  if  $A_1$  disappears in a subsequent reaction whose speed is greater than that of the reaction measured.  $C_1$ , etc., represent the initial concentrations in moles per liter;  $s$  is the speed of reaction;  $K$  is a constant of proportionality; and  $x$  is a concentration term of such magnitude that  $n_1'x$  is the number of molecules of  $A_1$  that have disappeared from one liter in time  $t$ . When applied to the speeds of the opposing reactions of a reversible process, this formula gives the same result for the equilibrium constant as that derived by thermodynamics.

The speed of reaction in liquid systems, however, is treated only by analogy. From van't Hoff's classic exposition of the similarity of *dilute* solutions to perfect gases, Equation 1 has been extended to *all* solutions. Historically, this formula was arrived at empirically by Wilhelm<sup>4</sup> for this same reaction long before van't Hoff's theories, but the great success of these simple views is responsible for its retention long after it had been found not to fit the facts.

Thermodynamics requires that the general expression for the equilibrium constant be in terms of the activities as defined by Lewis.<sup>10</sup> Since the ratio of the speeds of the opposing reactions of a reversible process must give the same equilibrium constant, it is a much more logical analogy to express the speed of a reaction (in a homogeneous system) in terms of activities. That is, the speed of any reaction in a homogeneous system is proportional to the activity of each reacting molecular species raised to the power which represents the number of molecules of that species which enter into the reaction according to the chemical equation. Lewis and Randall<sup>12</sup> have recently stated that this is a thermodynamic necessity for any reaction near equilibrium conditions.

<sup>12</sup> G. N. Lewis and M. Randall, *THIS JOURNAL*, **43**, 1150 (1921).

If we take the same chemical reaction as for Equation 1, the formula for the speed of reaction would be given by

$$s = K a_1^{n_1} a_2^{n_2} a_3^{n_3} \quad (2)$$

where  $a_1$ , etc., represent the activities of the various reactants, and the other symbols have the same meaning as before. Since we already have an undetermined factor of proportionality we can use relative activities, assigning unit activity to any desired state. However, we encounter difficulty in interpreting the quantity  $s$ . It must be measured by the number of molecules which react in unit time, but in what units should it be expressed? The answer to this question will be made simpler by the introduction of a new term—"semi-ideal solution."

By semi-ideal solution will be meant one in which the polarity or thermodynamic environment is independent of the concentration; it differs from an ideal solution in that there may be chemical reactions between the components, although it includes ideal solutions as a special case. A semi-ideal solution might also be called physically ideal, since all the variations from ideality are due to chemical changes. The chief characteristic of a semi-ideal solution is that the activity of each component is proportional to the molar fraction of that component which actually exists in the solution. Neither the number of moles of any component nor the total number of moles can be determined from the quantities added to the solutions; but, in many cases, the actual calculation of these quantities is unnecessary. The assumption of semi-ideality is customarily made in treating chemical action in solution, be it dissociation, association or compound formation, when the solution is considered as too concentrated for the simple laws of dilute solutions. Dolezalek<sup>13</sup> has gone so far as to claim that all solutions fulfil this condition. It is probable that most solutions are so nearly semi-ideal that the deviation from equality between activity and molar fraction is small.

For such solutions, as for ideal solutions, the quantity which is analogous to the volume of a perfect gas system is one mole of total substance, or the volume containing one mole. Replacing the total volume of a perfect gas system by the volume containing one mole of a semi-ideal liquid system is, at least approximately, the same as correcting the volume for the space occupied by all the molecules. If the polarity of the various kinds of molecules is the same, the forces of attraction and the distances between molecules will be independent of the nature of the molecules. Therefore the space between them will be approximately the same for any given number of molecules regardless of their size. But the space between the molecules is the free space, or the volume corrected for that part of it occupied by all the molecules, solvent as well as solutes. Then a dilute

<sup>13</sup> F. Dolezalek, *Z. physik. Chem.*, **64**, 727 (1908); see, however, J. J. vanLaar, *ibid.*, **72**, 723 (1910), and J. H. Hildebrand, *THIS JOURNAL*, **38**, 1457 (1916).

solution would be one in which the free volume is proportional to the total volume. If we must give up our picture of rigid molecules, and consider them as fields of force without any definite boundary where they can be said to end, this is probably as definite an idea of free space in a liquid system as we can obtain.

Pursuing our analogy to a perfect gas, we will consider that the speed  $s$  is measured by the number of molecules transformed in unit time in a volume which contains one mole of total substance. If  $x$  is the number transformed in time  $t$  in one liter, then  $s = \frac{1}{\Sigma C} \times \frac{dx}{dt}$ , where  $\Sigma C$  is the total number of moles per liter. Let us consider the special simple case where  $x$  is measured for the substance  $A_3$ , for which the solution is semi-ideal and for which  $n_3$  is equal to unity. The activity of  $A_3$  is  $a_3 = (C_3 - x)/\Sigma C$ , and Equation 2 becomes

$$s = \frac{1}{\Sigma C} \times \frac{dx}{dt} = K a_1^{n_1} a_2^{n_2} \left( \frac{C_3 - x}{\Sigma C} \right) \\ \text{or } dx/dt = K a_1^{n_1} a_2^{n_2} (C_3 - x). \quad (3)$$

It will be noted that  $a_1$  and  $a_2$  will in general be functions of the time or of  $x$ . For the third component we have reduced the formula to the same type as for perfect gases. If we can determine the functional relationship between  $a_1$ ,  $a_2$  and  $x$ , we will not be restricted to solutions which are semi-ideal to more than one component. Obviously for dilute solutions, where the activity is proportional to the concentration, Equation 3 reduces to Equation 1.

We have now an expression for the speed of reaction in terms of thermodynamic quantities. It is not, of course, a thermodynamic theory of chemical kinetics, for the equation is derived only by a reasonable analogy.

### The Inversion of Sucrose.

The inversion of sucrose as catalyzed by the hydrogen ion involves three reactants, sucrose, water and the hydrogen ion. If our formula is correct, its formulation when measured by the disappearance of sucrose is (from Equation 3),

$$dx/dt = K a_w^{n_w} a_h^{n_h} (C_s - x) \quad (4)$$

where the subscript (w) refers to water; the subscript (h) to the hydrogen ion and the subscript (s) to sucrose.

We can learn much about this reaction from the fact that, starting with any given concentration of sucrose and acid, the reaction gives a constant for a unimolecular reaction as measured by the disappearance of sucrose. Expressed mathematically,

$$\frac{dx}{dt} = k(C_s - x), \text{ or } k_s = \frac{1}{t} \ln \frac{C_s}{C_s - x}; \quad (5)$$

$k$  is the  $K_{uni}$  of Jones and Lewis, and is constant only for a single con-

centration of sugar and acid. The fact that  $k$  so determined is a constant shows that  $n_s$  is equal to unity, and that, for the special case where each molecule of sucrose which disappears is replaced by one of glucose and one of fructose, we are justified in replacing the activity of sucrose by its concentration. This is a matter of some importance since we have no direct means of measuring the activity of the sucrose. It also shows that the activities of the water and of the hydrogen ion may be considered as remaining constant during the course of the reaction. For the present we will assume that we can employ the same measure of the speed of reaction when the original concentration of the sugar is varied, and we will leave the justification of that assumption until we discuss the mechanism of the reaction.

The results of Palmaer<sup>14</sup> on solutions so dilute that the activity of the hydrogen ion is proportional to its concentration indicate that the speed of reaction is proportional to the first power of the hydrogen ion activity, or that  $n_h$  is also equal to unity. Unpublished work of Fales and Vosburgh and of Fales and Morrell, in which the activity of the hydrogen ion was measured directly, shows that this is also the case in the higher concentrations as studied by Jones and Lewis, and also shows that the hydrogen-ion activity does actually remain constant during the course of the reaction.

With these simplifications, Equation 4 becomes

$$dx/dt = K a_w^{n_w} a_h (C_s - x) \quad (6)$$

where  $x$  and  $t$  are the only variables. Integrating, this becomes

$$K = \frac{1}{a_w^{n_w} a_h} \times \frac{1}{t} \ln \frac{C_s}{C_s - x} \quad (7)$$

Comparing Equations 5 and 7, we see that

$$K = k / a_w^{n_w} a_h \quad (8)$$

If we can measure  $k$ ,  $a_w$ , and  $a_h$ , we can determine the value of  $n$  which gives a constant value of  $K$ , and so determine the number of molecules of water which enter into the reaction. Jones and Lewis<sup>11</sup> have measured  $k$  and  $a_h$  for solutions containing 10, 20, 30, 40, 50, 60 and 70 g. of sucrose per 100 cc. of solution and 0.1  $N$  with respect to sulfuric acid at 20° and at 40°. They have expressed the activity in terms of moles of hydrogen ion per liter; but, in order not to change the magnitude of our constants more than necessary, we will adopt the convention that the activity of the hydrogen ion in 0.1  $N$  solution of sulfuric acid in water alone is unity.

The activity of the water can be interpolated from the vapor-pressure measurements of Berkeley, Hartley and Burton.<sup>15</sup> Water vapor at or

<sup>14</sup> W. Palmaer, *Z. physik. Chem.*, **22**, 493 (1897).

<sup>15</sup> Earl of Berkeley, E. G. J. Hartley and C. V. Burton, *Phil. Trans.*, **218A**, 295 (1919).



below room temperature behaves so nearly like a perfect gas that the vapor pressure of an aqueous solution may be taken as an exact measure of the activity of the water in that solution. These authors have measured very accurately the vapor pressures relative to that of pure water at the same temperature. If we adopt the convention that the activity of pure water is unity, these measurements give directly the relative activities required.

**The Activity of the Water.**—The method of determining the activity of the water is given in considerable detail since other workers might wish to use the same method.

The first step is to interpolate to the concentrations used by Jones and Lewis, but still at 0° and 30°, the temperatures of the vapor-pressure measurements. To do this the concentrations of Jones and Lewis are recalculated in terms of g. of sucrose per 100 g. of water by using the number of moles of water per liter given in their paper. The interpolation was then made graphically by two methods: in the first the activity was plotted against the concentration; in the second the ratio,  $(1-a_w)/\text{conc.}$ , was plotted against the concentration. Each of these methods gave a graph of but slight curvature. Each curve was plotted twice on different scales, and the mean of the four determinations was taken as the best value. The greatest deviation of any individual value from this mean is 0.04% and the average deviation is less than 0.015%. The values of the activity used in plotting the curve are given in Table II (p. 2410) of the following article.

To determine the activities at 20° and at 40° from those at 0° and at 30°, the assumption is made that the relative activity is a linear function of the temperature. Since the maximum difference between 0° and 30° is 0.3%, this assumption cannot introduce an appreciable error. Table I gives the interpolated values at all four temperatures for solutions containing the same quantities of sugar as those used by Jones and Lewis but without sulfuric acid.

TABLE I.

INTERPOLATED ACTIVITIES OF WATER IN AQUEOUS SUGAR SOLUTIONS.

Concentration.		Activity ( $a$ ).			
G. of sugar per 100 cc.	100 g. of water.	0°.	30°.	20°.	40°.
0	0.0	1.0000	1.0000	1.0000	1.0000
10	10.70	0.9940	0.9944	0.9943	0.9945
20	22.93	0.9868	0.9875	0.9873	0.9877
30	37.05	0.9782	0.9791	0.9788	0.9794
40	53.39	0.9676	0.9687	0.9683	0.9691
50	72.93	0.9539	0.9552	0.9548	0.9556
60	96.37	0.9360	0.9377	0.9371	0.9383
70	125.70	0.9119	0.9149	0.9139	0.9150

It is next necessary to correct the activity of the water for the sulfuric acid present. There are no data available for the temperatures in question, but the decrease in activity is so small that we are justified in assuming that it does not change with the temperature and in calculating it from the freezing-point depression. Noyes and Falk<sup>16</sup> give the best value for the freezing-point depression of 0.05 *M* sulfuric acid as 0.2056°. Using the formula of Washburn<sup>17</sup> quoted by these same authors,  $1 - a_w = (p_0 - p)/p_0 = 0.00969 \Delta t (1 - 0.0043 \Delta t)$ , we obtain  $1 - a_w = 0.0021$ . This holds for zero sugar concentration.

The next step is to calculate the decrease in solutions containing sucrose. The most obvious assumption is the ordinary one for dilute solutions, that the decrease due to the sulfuric acid is the same for all solutions. This assumption undoubtedly gives too small values for the decrease, but calculations are made on this basis and will be designated as results according to the first assumption.

A better value can be obtained by treating the sugar solutions as semi-ideal solutions in which the degree of the ionization of the sulfuric acid is independent of the sugar concentration, the degree of association of the water is constant, and there is no polymerization of any other substance. Our symbols will be the same as before with the addition that:  $C_w$ ,  $a_w$ , etc., apply to solutions containing both sugar and acid;  $C'_w$ ,  $a'_w$ , etc., to solutions of sugar without acid;  $C''_w$ ,  $a''_w$ , etc., to solutions of acid without sugar; the subscript (<sub>w</sub>) to monohydrol and the subscript (<sub>p</sub>) to polymerized water;  $N_o$  is the molar fraction of monohydrol in pure water.

The sucrose in solution may be partially hydrated and partially not, but the total concentration of all its forms will be the amount of sucrose added per liter,  $C_s$ . The sulfuric acid will exist as  $H_2SO_4$ ,  $HSO_4^-$ ,  $SO_4^{--}$  and  $H^+$ , any one of which may be hydrated to various degrees. But the sum of the first three will always equal the quantity of sulfuric acid added, 0.05 moles per liter; the quantity of hydrogen ion per liter will be  $C_h$ . The activity of monohydrol in pure water is one, but its molar fraction is  $N_o$ . So in any solution the activity of monohydrol is equal to the molar fraction divided by  $N_o$ . The molar fraction of polymerized water in pure water is  $1 - N_o$ . Since the ratio of molar fractions of monohydrol and polymerized water is constant, the following holds true for all solutions.

$$\frac{C_p}{C_w} = \frac{N_p}{N_w} = \frac{1 - N_o}{N_o}, \quad C_p = \frac{C_w(1 - N_o)}{N_o} \quad \text{and} \quad C_p + C_w = C_w/N_o$$

The total number of moles per liter will be,

$$C_w + C_p + C_h + C_s + 0.05 = C_w/N_o + C_h + C_s + 0.05.$$

From the hypothesis that the activity of each substance is equal to its molar fraction we have,

<sup>16</sup> A. A. Noyes and K. G. Falk, *THIS JOURNAL*, 32, 1013 (1910).

<sup>17</sup> E. W. Washburn, *Technology Quart.*, 21, 373 (1908).

$$\begin{aligned}
\frac{C_w/N_o N}{C_w/N_o + C_s} &= a'_w; \quad \frac{C'_w N_o}{C'_w/N_o + C_h + 0.05} = a''_w; \quad \frac{C_h}{C'_w/N_o + C_h + 0.05} = a''_h; \\
\frac{C_w/N_o}{C_w/N_o + C_h + C_s + 0.05} &= a_w; \quad \frac{C_h}{C_w/N_o + C_h + C_s + 0.05} = a_h \\
\text{since } \frac{C'_s}{C'_w/N_o} &= \frac{C_s}{C_w/N_o}, \text{ and } C'_h = C_h, \\
1 - a''_w &= 1 - \frac{C'_w/N_o}{C'_w/N_o + C_h + 0.05} = \frac{C_h + 0.05}{C'_w/N_o + C_h + 0.05} \\
a'_w - a_w &= \frac{C_w/N_o}{C_w/N_o + C_s} - \frac{C_w/N_o}{C_w/N_o + C_h + C_s + 0.05} \\
&= \frac{C_w/N_o (C_h + 0.05)}{(C_w/N_o + C_s)(C_w/N_o + C_h + C_s + 0.05)} \\
&= \frac{C_w/N_o}{C_w/N_o + C_s} \times \frac{C_h + 0.05}{C_w/N_o + C_h + C_s + 0.05} \\
&= \frac{C_w/N_o}{C_w/N_o + C_s} \times \frac{C_h + 0.05}{C'_w/N_o + C_h + 0.05} \times \frac{\frac{C_h}{C'_w/N_o + C_h + 0.05}}{\frac{C_h}{C'_w/N_o + C_h + 0.05}} \\
&= a'_w \times (1 - a''_w) \left( \frac{a_h}{a''_h} \right) \quad (9)
\end{aligned}$$

or the decrease in the activity of the water in a sugar solution due to the sulfuric acid is equal to the decrease in the solution without sugar multiplied by the activity of the water in the sugar solution without acid and by the activity of the hydrogen ion in the final solution relative to that of an acid solution of the same concentration in the absence of sugar. Table II gives the activity of the hydrogen ion in the various solutions relative to that of 0.1 *N* sulfuric acid in pure water as unity, and the decrease in the activity of the water due to the sulfuric acid as calculated by Equation 9. Probably this decrease is a trifle too large. We will find later that the sugar solutions behave like semi-ideal solutions in which the degree of ionization of the sulfuric acid increases a little with increasing sugar concentration; and, assuming that whatever causes the apparent increased ionization would have the same effect on the activity of the water as though the increase were real, this would tend to give values for the decrease a little too large. Values calculated from these decreases are designated as results according to the second assumption.

The values of the activity of the water used in Tables III, etc., are rounded off to three places. The calculations are made on both assumptions since the true value probably lies between the two. The author believes that the final values of the activity as calculated by the second assumption are correct to one or two parts per thousand.

TABLE II.  
DECREASE IN ACTIVITY OF WATER DUE TO SULFURIC ACID ACCORDING TO EQUATION 9.

Conc.	20°.		40°.	
	Activity of H <sup>+</sup> . $a_h/a^*h.$	Decrease. $a'_w - a_w.$	Activity of H <sup>+</sup> . $a_h/a^*h.$	Decrease. $a'_w - a_w.$
0	1.00	0.0021	1.00	0.0021
10	1.13	0.0024	1.12	0.0023
20	1.30	0.0027	1.24	0.0026
30	1.49	0.0031	1.56	0.0032
40	1.75	0.0036	1.82	0.0037
50	1.97	0.0039	2.18	0.0044
60	2.32	0.0046	2.60	0.0051
70	2.70	0.0052	3.04	0.0058

It is interesting to compare the calculated decrease in activity with the measurements of Rivett<sup>18</sup> on the effects of various salts. Rivett measured the freezing points of 77 solutions of 14 salts in concentrations ranging from 0.1 *N* to *N* with respect to the salt and up to 40 g. of sugar per 100 g. of water. The different salts should not be expected to behave exactly like the sulfuric acid, but might be expected to have a somewhat similar behavior. The relative depression in the presence and in the absence of sugar is within the limits set by our two assumptions in all but 10 cases. Of these 5 are apparently errors in measurement or in tabulation, since they differ widely from the other results on the same salts. The other 5 are concentrated copper sulfate solutions, which appear to give regularly higher values than the sulfuric acid. The 67 values which fall within the limits are distributed nearly uniformly between the two.

**The Order of the Reaction with Respect to the Water.**—To determine the number of water molecules which enter into the reaction, we use Equation 8 and substitute various integral values for  $n_w$  to determine which will give constant values of  $K$  independent of the sugar concentration. Tables III A and IV A gives these values at 20° and 40° according to the first assumption.  $K_1$  is the value of  $K$  when  $n_w$  equals 1;  $K_5$  when  $n_w$  equals 5, etc. Tables III B and IV B give the corresponding results when  $a_w$  is calculated according to the second assumption. The values of  $k$  and  $a_h$  are, of course, the same for either assumption. In the B tables,  $C_w$  is the concentration of water divided by that in 0.1 *N* sulfuric acid without sugar—the relative concentration of the water—and  $K_c$  in the last column is  $\frac{k}{a_h \times C_w}$ . This is the value of  $K$  derived by Jones and Lewis multiplied by the number of moles per liter of water and of hydrogen ion in 0.1 *N* sulfuric acid without sugar; these values are included for comparison.

It is evident that when  $n_w=1$ , the values of  $K$  decrease rapidly with increasing sugar concentration. It is necessary to raise the activity of

<sup>18</sup> A. C. D. Rivett, *Medd. K. Vetenskapsakad. Nobelinst.*, 2, No. 9 (1911).

the water to a much higher power. The results are tabulated for  $n_w = 5$ , 6 and 7. The values of  $K_5$  still decrease, those of  $K_7$  increase, while those of  $K_6$  remain sensibly constant.

The average values of the  $K$ 's are given, and the square root of the mean of the squares of the deviations of the individual values from the average value is given in the row designated R. M. S. D. (root mean square deviation). This is the best method of determining constancy. The values for zero concentration of sugar are given in parentheses, but they are not used in calculating the average values since the corresponding value of  $k$  is obtained by extrapolation.

TABLE III A.  
VALUES OF  $K$  AT 20° BY FIRST ASSUMPTION.

Conc.	$k \times 10^4$	$a_h$	$a_w$	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_3 \times 10^4$	$K_7 \times 10^4$
0	(4.14)	1.00	0.998	(4.15)	(4.18)	(4.19)	(4.20)
10	4.43	1.13	0.992	3.94	4.07	4.10	4.13
20	4.79	1.30	0.985	3.74	3.97	4.03	4.10
30	5.21	1.49	0.977	3.57	3.92	4.02	4.11
40	5.54	1.75	0.966	3.28	3.76	3.90	4.03
50	5.95	1.97	0.953	3.17	3.85	4.04	4.24
60	6.22	2.32	0.935	2.87	3.76	4.02	4.30
70	6.29	2.70	0.912	2.55	3.69	4.05	4.44
Average					3.86	4.02	4.19
R.M.S.D.					0.127	0.057	0.131

TABLE III B.  
VALUES OF  $K$  AT 20° BY SECOND ASSUMPTION.

Conc.	$a_w$	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_3 \times 10^4$	$K_7 \times 10^4$	$C_w$	$K_c \times 10^4$
0	0.998	(4.15)	(4.18)	(4.19)	(4.20)	1.000	(4.14)
10	0.992	3.94	4.07	4.10	4.13	0.935	4.18
20	0.985	3.74	3.97	4.03	4.10	0.872	4.22
30	0.976	3.58	3.94	4.04	4.14	0.810	4.31
40	0.965	3.28	3.78	3.92	4.06	0.749	4.23
50	0.951	3.18	3.89	4.09	4.30	0.686	4.41
60	0.933	2.88	3.80	4.07	4.36	0.623	4.31
70	0.909	2.56	3.75	4.13	4.54	0.557	4.18
Average			3.89	4.05	4.23		4.26
R.M.S.D.			0.108	0.063	0.161		0.078

TABLE IV A.  
VALUES OF  $K$  AT 40° BY FIRST ASSUMPTION.

Conc.	$k \times 10^4$	$a_h$	$a_w$	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_3 \times 10^4$	$K_7 \times 10^4$
0	(5.98)	1.00	0.998	(5.99)	(6.04)	(6.05)	(6.06)
10	6.73	1.12	0.992	6.06	6.26	6.31	6.36
20	7.37	1.24	0.986	6.03	6.38	6.47	6.56
30	8.04	1.56	0.977	5.28	5.79	5.93	6.07
40	8.80	1.82	0.967	5.00	5.72	5.91	6.12
50	9.53	2.18	0.954	4.58	5.53	5.80	6.08
60	10.22	2.60	0.936	4.20	5.47	5.85	6.25
70	10.92	3.04	0.914	3.93	5.63	6.16	6.74
Average					5.83	6.06	6.31
R.M.S.D.					0.330	0.237	0.239

TABLE IV B.  
 VALUES OF  $K$  AT 40° BY SECOND ASSUMPTION.

Conc.	$a_w$	$K_1 \times 10^5$	$K_5 \times 10^5$	$K_6 \times 10^5$	$K_7 \times 10^5$	$C_w$	$K_c \times 10^5$
0	0.998	(5.98)	(6.04)	(6.05)	(6.06)	1.000	(5.98)
10	0.992	6.06	6.26	6.31	6.36	0.935	6.43
20	0.985	6.03	6.41	6.51	6.61	0.872	6.81
30	0.976	5.28	5.82	5.96	6.11	0.810	6.36
40	0.965	5.01	5.78	5.99	6.20	0.749	6.45
50	0.951	4.60	5.62	5.91	6.21	0.686	6.38
60	0.933	4.21	5.56	5.96	6.39	0.623	6.31
70	0.910	3.95	5.76	6.33	6.95	0.557	6.45
	Average		5.89	6.12	6.40		6.46
	R.M.S.D.		0.298	0.222	0.269		0.152

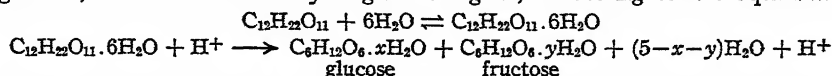
It is clear that the values of  $K_6$  are much more nearly constant than those of  $K_5$  or  $K_7$ , and this conclusion is independent of the assumption as to the effect of the acid on the activity of the water, showing that a small error introduced by these assumptions will not affect the conclusions. The results at 40° are not so sharply conclusive as those at 20°. Apparently the experimental results are considerably less accurate due to the greatly increased speed of reaction, and the experimental errors introduce a variation of nearly the same magnitude as the differences between the results for  $K_5$ ,  $K_6$  and  $K_7$ . However,  $K_6$  is still the best constant.

These results show conclusively that, if our conception of the speed of reaction is correct, a large number of molecules of water enter into the reaction. In order to establish that this number is 6 rather than 5 or 7 and that the number is independent of the sugar concentration, etc., a larger number of experiments with various acids at different concentrations will be necessary. Professor Fales has kindly consented to direct his work on sucrose inversion to a thorough test of the theory. To make the following discussion clearer we will assume that 6 molecules of water enter into the reaction, while we recognize that more complete results may change this number slightly. But such a change will not greatly change the nature of the discussion. If it be found that 7 molecules react rather than 6, the discussion will hold true if 7 be substituted for 6 wherever it occurs.

**The Mechanism of the Reaction.**—With 6 molecules of water taking part in the reaction, the number of possible ways of picturing the mechanism is very large. It seems probable, however, that the activity of the hydrogen ion in catalysis is the same as its activity measured by the hydrogen electrode. Then the 6 water molecules must react with the sugar or with a complex of sugar and the hydrogen ion. Jones and Lewis come to the conclusion that the sucrose and the hydrogen ion react to form a complex ion which then reacts with the water according to the equation,

$$C_{12}H_{22}O_{11} + H^+ \rightleftharpoons C_{12}H_{22}O_{11} \cdot H^+; \quad C_{12}H_{22}O_{11} \cdot H^+ + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} + H^+.$$

If a large number of water molecules react instead of only one, this mechanism shows no reason why it should be 6 independent of the temperature and sugar concentration. The saccharated hydrogen ion also seems improbable, because, if it existed in the solution to any extent, it should reduce the activity of hydrogen ion in concentrated sugar solutions. It is much more probable that the water molecules react with the sugar first, and that this hydrate of sucrose then reacts with a hydrogen ion to give glucose, fructose and the hydrogen ion again, according to the equation:



These results cannot show whether the action of the hydrated sugar and the hydrogen ion is to form an intermediate complex ion or not.

**The Activity of the Sugar.**—If this picture of the mechanism of the reaction is correct, the reaction whose speed we are really discussing is the disappearance of the anhydrous (unhydrated) sugar. Also, if the measurements of the extent of hydration<sup>19</sup> in the following paper are even approximately correct, we cannot assume that the sugar is almost all either hydrated or unhydrated; but both forms exist in our solutions to a considerable extent and their relative quantities vary widely with the concentration. It is necessary, then, to question critically our use of the disappearance of total sugar as a measure of the speed of reaction.

We will let the subscript (anh) apply to the anhydrous (unhydrated) sugar, and the subscript (hyd) apply to the hydrate. Then  $C_s = C_{anh} + C_{hyd}$ , and similarly for the other properties. The equations we used as a measure of the speed of reaction are

$$\frac{dx}{dt} = K a_w^n a_h (C_s - x), \quad (6)$$

$$\text{and} \quad K = \frac{1}{a_w^n a_h} \times \frac{1}{t} \ln \frac{C_s}{C_s - x}. \quad (7)$$

The corresponding equations for the disappearance of anhydrous sugar are

$$dy/dt = K a_w^n a_h (C_{anh} - y), \quad (10)$$

$$\text{and} \quad K = \frac{1}{a_w^n a_h} \times \frac{1}{t} \ln \frac{C_{anh}}{C_{anh} - y} \quad (11)$$

where  $y$  is the quantity of anhydrous sugar which disappears from one liter in time  $t$ .

$$\text{The } K\text{'s will be identical in case } \frac{C_s - x}{C_s} = \frac{C_{anh}}{C_{anh} - y}. \quad (12)$$

Let us consider the hydration of sucrose from the viewpoint of the law of mass action expressed in terms of activities, the holding of which is a thermodynamic necessity if the substances exist at all.

<sup>19</sup> "Extent of hydration" is used to indicate the fraction of the sugar molecules hydrated; "degree of hydration," the number of molecules of water combined with one of sugar in the hydrate.

$$K_{\text{hyd}} = \frac{a_{\text{hyd}}}{a_{\text{anh}} \times a_w^6}, \text{ or } \frac{a_{\text{hyd}}}{a_{\text{anh}}} = K_{\text{hyd}} a_w^6 \quad (13)$$

$$\frac{a_{\text{hyd}} + a_{\text{anh}}}{a_{\text{anh}}} = \frac{a_s}{a_{\text{anh}}} = 1 + K_{\text{hyd}} a_w^6. \quad (14)$$

If, during the course of a single reaction, the activity of the water is constant, the right-hand side and therefore the left-hand side of Equation 14 will be constant. Now let us assume that the solutions are semi-ideal with respect to the hydrated and unhydrated sugar. Then for the activities we may substitute molar fractions, and we have,

$$\text{const.} = \frac{a_s}{a_{\text{anh}}} = \frac{N_s}{N_{\text{anh}}} = \frac{\frac{C_s}{\Sigma C}}{\frac{C_{\text{anh}}}{\Sigma C}} = \frac{C_s}{C_{\text{anh}}}. \quad (15)$$

If we substitute the values of  $C$  at time zero and time  $t$ , we have,

$$\frac{C_s}{C_{\text{anh}}} = \frac{C_s - x}{C_{\text{anh}} - y}, \text{ or } \frac{C_s}{C_s - x} = \frac{C_{\text{anh}}}{C_{\text{anh}} - y},$$

which is identical with Equation 12. We are therefore justified in taking the rate of disappearance of the total sucrose as a measure of the speed of disappearance of anhydrous sucrose when the activity of the water remains constant.

But the assumption of constant activity of the water is not in accord with experiment. Invert sugar depresses the activity of water very nearly twice as much as the sucrose from which it is derived, and this fact has been used to follow the course of the reaction by the change in boiling point<sup>20</sup> and in freezing point.<sup>21</sup> For the most concentrated solutions the activity of the water would be reduced about 1/10 during the course of the reaction. This would mean that our integration of Equations 6 and 10 with the assumption of constant activity of the water is not exact. Equations 14 and 15 still hold, however, and combining them we have,

$$C_s/C_{\text{anh}} = 1 + K_{\text{hyd}} a_w^6 \quad (16)$$

Then, as the activity of the water decreases, the ratio of anhydrous to total sugar will increase. This will cause an acceleration of the reaction when measured in terms of the disappearance of total sugar (Equation 6) which will tend to compensate for the retardation due to the decreased activity of the water, and there will be a smaller error in assuming the activity of the water to be constant than if Equation 10 itself were used.

It does not seem worth while to follow the analysis of this factor more rigorously, since there are at least two other factors which tend to produce a variation in  $k$  as determined by the optical rotatory power. The first

<sup>20</sup> J. E. Trevor and F. C. Kortright, *Z. physik. Chem.*, **14**, 149 (1894).

<sup>21</sup> L. Kahlenberg, D. J. Davis and R. E. Fowler, *THIS JOURNAL*, **21**, 1 (1899).



is the mutarotation of the products of inversion;<sup>22</sup> the second, the reversion<sup>23</sup> or slow change in the final rotation which makes it difficult to determine the true end-point. This reversion is apparently due, in part at least, to a recombination of the glucose and fructose to disaccharides other than sucrose.

Worley made some very careful measurements and determined the change in  $k$  with time by using Equation 5 integrated between the limits  $t_1$  and  $t_2$ , which gives the formula,

$$k = \frac{1}{t_2 - t_1} \ln \frac{C_s - x_1}{C_s - x_2} \quad (17)$$

This formula has the single disadvantage that it multiplies the experimental error, since the time intervals must always be small. Worley found that for his experiments the total effect of the interfering factors was to give increasing values of  $k$ , while the decrease in the activity of the water would tend to give decreasing values.

Our problem is not to determine the exact kinetics of this reaction, actually of the eighth order and complicated by subsequent reactions, but simply to ascertain whether the value of  $k$  as calculated from the experimental results is really the  $k$  we have used in Equation 8. This will be true if the experimental  $k$  is the initial  $k$ —that at the beginning of the reaction—when the activity of the water has not appreciably changed and may be regarded as constant. A sufficient condition will be that  $k$  as determined by Equation 17 does not vary during the reaction.

Jones and Lewis give only one pair of results from which this condition may be tested, those for 70 g. of sucrose at 40°. These results are, however, the ones most likely to give a variation in  $k$ , since the activity of the water changes most for the concentrated solutions. Table V gives the constants for two duplicate experiments calculated by Equation 17 and by Equation 5. Those by Equation 17 are tabulated in the same row as  $t_2$ , while  $t_1$  is the next preceding time. It will be seen that the value of  $k$  from Formula 17 shows no systematic trend and that the average is practically the same as that calculated from Formula 5. Due to the magnification of the experimental errors with the shorter time intervals, the variation in the individual values is considerably greater for Formula 17. The results show that we are justified in using in Equation 8 the values of  $k$  as measured by Jones and Lewis.

<sup>22</sup> J. Meyer, *Z. physik. Chem.*, **62**, 59 (1908); **72**, 117 (1910).

C. S. Hudson, *THIS JOURNAL*, **30**, 1160 (1908); **32**, 885 (1910).

<sup>23</sup> A. Wohl, *Ber.*, **23**, 2084 (1890). E. Fischer, *ibid.*, **23**, 3687 (1890).

F. P. Worley, *J. Chem. Soc.*, **99**, 349 (1911); *Proc. Roy. Soc. (London)*, **87A**, 555 (1912).

TABLE V.  
RATE OF INVERSION OF SUCROSE.  
70 g. per 100 cc. at 40°.

Expt. 1.			Expt. 2.		
Time Sec.	Eq. 5. $k \times 10^3$	Eq. 17.	Time. Sec.	Eq. 5. $k \times 10^3$	Eq. 17.
780	10.82	.....	1200	10.81	.....
1500	11.03	11.25	1950	10.81	10.81
2100	10.98	10.87	2460	10.83	10.90
3060	11.00	11.04	3060	10.77	10.52
3900	11.03	11.13	3960	10.89	11.30
5160	11.07	11.20	4440	10.86	10.63
6420	11.11	11.28	6360	10.96	11.20
7500	10.98	10.20	6900	10.97	11.07
Av.	11.00	11.00	Av.	10.86	10.92
Reaction 55% complete.			Reaction 53% complete.		

The Activity of the Hydrogen Ion.—Jones and Lewis account for the increased activity of the hydrogen ion in the concentrated sugar solutions by a difference in the catalytic environments of sucrose and of water. Since the activity (as measured by the catalytic effect) does not change during the course of the reaction, the catalytic effect of the sucrose must be the same as that of the corresponding amount of invert sugar, and they therefore assume that it is zero, and that the whole change is due to the negative catalytic effect of the water. This they find expressible as an exponential function of the water concentration.

A very simple explanation is obtained from the view of semi-ideal solutions. If this view is correct, the activity of the hydrogen ion is proportional to its molar fraction, and the great change with changing sugar concentration is due to a change in the number of total moles per liter. By using the activity of the water and that of the hydrogen ion and applying the concept of a semi-ideal solution in which the degree of association of the water remains constant and no other substances are polymerized, it is possible to calculate the concentration of hydrogen ions in moles per liter. For the water we have,

$$\frac{C_w/N_o}{C_w/N_o + C_h + C_s + 0.05} = a_w; C_w/N_o = \frac{a_w}{1-a_w} (C_h + C_s + 0.05).$$

According to our convention, the activity of the hydrogen ion is not equal to its molar fraction, since we have assigned unit activity, not to a solution of unit molar fraction, but to a water solution of 0.1 *N* sulfuric acid. However, the activity will be proportional to the molar fraction, and we will let *K* be the proportionality constant.

$$\frac{C_h}{C_w/N_o + C_h + C_s + 0.05} = K a_h$$

Substituting the value of  $C_w/N_o$  obtained above and solving for  $C_h$ , we have

$$C_h = \frac{K a_h}{1-a_w-K a_h} (C_s + 0.05). \quad (18)$$

The value of  $K$  may be obtained for each temperature by solving the equation for the solution without sugar where the hydrogen-ion concentration is known. At  $20^\circ$ ,  $C_h=0.06$ ,  $a_h=1$ ,  $a_w=0.998$ ,  $C_s=0$ ; at  $40^\circ$ ,  $C_h=0.05$  and the others have the same values as at  $20^\circ$ . Table VI gives the values of the hydrogen-ion concentration calculated from Equation 18 at  $20^\circ$  and at  $40^\circ$ . In each case the values are calculated according to both assumptions as to the effect of the sulfuric acid on the activity of the water. The fact that the results are only a few per cent. different in the two cases shows that, even though the form of the mathematical equations is similar to those used in calculating the change in activity according to the second assumption, the results cannot depend upon that assumption.

TABLE VI.

CONCENTRATION OF HYDROGEN IONS IN AQUEOUS SUGAR-SULFURIC ACID SOLUTIONS.

Conc. of sugar.	20°.		40°.	
	1st assumpt.	2nd assumpt.	1st assumpt.	2nd assumpt.
0	0.060	0.060	0.050	0.050
10	0.062	0.062	0.056	0.056
20	0.066	0.066	0.062	0.057
30	0.070	0.067	0.067	0.064
40	0.072	0.070	0.071	0.067
50	0.072	0.069	0.075	0.070
60	0.073	0.071	0.076	0.073
70	0.072	0.070	0.077	0.073

Since the solutions are 0.1  $N$ , multiplication of the hydrogen-ion concentration by 1000 will give the degree of ionization of the sulfuric acid in percentages. In each case the degree of ionization increases with increasing sugar concentration, but the increase is not very large, and for the more concentrated solutions it disappears within the rather large experimental error. This error is due to the fact that the hydrogen-ion concentration is calculated from small differences. A slight variation of the solutions from semi-ideality or a different assumption as to the degree of ionization without sugar would also change the table somewhat. If allowance were made for the smaller degree of association of the water in the solutions where its molar fraction is smaller, the concentration of hydrogen ion in the more concentrated solutions would be reduced. Certainly these results are too few for theorizing on the efficiency of water and of sugar solutions as ionizing media except to point out that they are not very different, and that we have eliminated the anomaly of an ionization greater than 100%.

Jones and Lewis reduced the negative catalytic effect of water on the inversion of sucrose as observed by Rosanoff and Potter<sup>24</sup> to a catalytic

<sup>24</sup> M. A. Rosanoff and H. M. Potter, *THIS JOURNAL*, 35, 248 (1913).

effect on the ionization of the acid. Our interpretation of the nature of sugar solutions reduces it to a difference in molar volume between sucrose and water. The fact that it may be expressed as an exponential function of the water concentration can give no new information on the nature of anticatalytic action.<sup>25</sup>

**The Relation to the Neutral Salt Effect.**—If this theory as to the dependence of the speed of reaction on the activities of the reactants is correct, the effect of a neutral salt on the speed of reaction should be a complicated one. The addition of a neutral salt will affect the activity of each component. The activity of the water will be decreased as is shown by the decrease of vapor pressure or corresponding change in the other colligative properties. The activity of the hydrogen ion will be increased, as has been shown by the work of many observers.<sup>26</sup> Most of these observers interpret the effect as due to a decrease in the apparent volume of the solvent. In the terms of our theory this would mean an increase in the molar fraction of the hydrogen ion due to a decrease in the number of moles of water. Lack of knowledge of the degree of dissociation of the added salts prevents an analysis of this effect similar to that made on the sugar solutions to determine whether these solutions may also be interpreted as semi-ideal.

The effect of the salt on the activity of the sucrose has never been measured, but it would probably increase it. By decreasing the activity of the water it would decrease the extent of hydration of the sucrose. It is also a general characteristic of salts that they increase the activity of organic

<sup>25</sup> A paper by Garner and Masson (*Phil. Mag.*, 41, 484-6 (1921)) on this subject has just come to the author's attention (September 29, 1921). They note that the ratio between the activity of hydrogen ions in a sugar solution and in pure water is approximately equal to the ratio between the osmotic pressure of the solution and that calculated by van't Hoff's Law and to the inverse ratio of the solubility of hydrogen in that solution and in pure water. They explain all three by the removal of water, probably to form a hydrate of sucrose. The assumptions upon which this is based for the solubility of gases are discussed in the following paper. For the osmotic pressure it must be assumed that the Morse formula gives an accurate expression for the osmotic pressure of an ideal solution; this is probably correct within the limits of their approximations. For the hydrogen ion activity one must assume that the activity of the hydrogen ion is inversely proportional to the quantity of water in which it is dissolved and independent of the other components of the solution. The present author can see no reason for assigning this unique position to water. It would certainly lead to astonishingly large results for the activity of hydrogen ion in nearly anhydrous alcohol or glycerine.

<sup>26</sup> G. Poma, *Z. physik. Chem.*, 88, 671 (1914).

H. S. Harned, *THIS JOURNAL*, 37, 2460 (1915).

H. A. Fales and J. M. Nelson, *ibid.*, 37, 2769 (1915).

A. W. Thomas and M. E. Baldwin, *ibid.*, 41, 1981 (1919).

J. A. Wilson, *ibid.*, 42, 715 (1920).

solutes, as shown by the decreased solubility and coefficient of partition with organic solvents.<sup>27</sup>

It will be necessary to include all these effects in the consideration of neutral salt action. This becomes particularly important in the determination of the catalytic effect of the non-ionized acid. If this is to be calculated from the change in catalytic effect with changing acid concentration or on the addition of neutral salts, all the factors must be taken into consideration. It is not sufficient to follow the customary procedure of assuming the activity of the water and of the substrate to remain constant and to calculate the activity of the hydrogen ion from the law of mass action in terms of concentrations. The writer does not desire to question the existence of a catalytic effect of non-ionized acid, which, for certain reactions, seems to be firmly based on a variety of grounds, but he does wish to question the ordinary methods of calculating the relative catalytic effect of non-ionized acid and hydrogen ion.

Arrhenius and Andersson<sup>9</sup> have studied the neutral salt effect on sucrose inversion from their viewpoint of osmotic pressures, and conclude that there is no evidence for a catalytic action of the un-ionized acid. Their osmotic pressure of the hydrogen ion is the same as its activity and is calculated with some extrapolation from the hydrogen-electrode measurements of Harned; the osmotic pressure of sugar they calculate from freezing-point measurements by a method which seems to me entirely unjustified; and they ignore the part of the water in the reaction. At present there are not enough data available for the analysis of this very important problem.

### Summary.

1. A method has been outlined for calculating the activity of water in sugar solutions of any concentration at temperatures near room temperature. The method has also been extended to solutions containing a small amount of other solute (sulfuric acid).

2. A formula for the speed of reaction in solutions in terms of the activities of the reactants is developed and suggested as the most logical formula for solutions.

3. By the application of this formula to the inversion of sucrose it is shown that the available data indicate that the reaction is of the sixth order with respect to water.

4. The results are interpreted as indicating the existence of a hexahydrate of sucrose.

5. The effect of the addition of sugar in increasing the activity of the hydrogen ion is explained as being very largely due to an increase in the

<sup>27</sup> For ethyl acetate: H. Lunden, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 15 (1911); for benzoic and salicylic acids: B. de Szyszkowski, *ibid.*, **2**, No. 41 (1913).

molar fraction of hydrogen ions without any large change in the actual degree of ionization.

6. A warning is given concerning the customary method of calculating the catalytic effect of un-ionized acid.

In conclusion the author wishes to express his hearty thanks to Professor H. A. Fales and Mr. J. C. Morrell for their courtesy in giving him access to unpublished work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE.]

## THE HYDRATION OF SUCROSE IN WATER SOLUTION AS CALCULATED FROM VAPOR-PRESSURE MEASUREMENTS.

BY GEORGE SCATCHARD.

Received, July 27, 1921.

### Introduction.

The determination of the existence of hydrates of sucrose in its aqueous solutions and the calculation of the average degree of hydration of the sucrose have been made from various properties of these solutions. Jones and Getman,<sup>1</sup> Callendar,<sup>2</sup> Washburn<sup>3</sup> and Bousefield<sup>4</sup> calculated the degree of hydration from the freezing point; Bousefield, Frazer and Myrick<sup>5</sup> and Porter<sup>6</sup> used the osmotic pressure; and Philip,<sup>7</sup> the solubility of hydrogen in sugar solutions. Einstein<sup>8</sup> concluded from a kinetic treatment of viscosity that the sugar must be very heavily hydrated, but he did not determine the degree.

The calculation of hydration from the solubility of a gas depends on two assumptions: that the power to dissolve hydrogen of a given mass of water is independent of anything with which it may be mixed, and that the dissolving power of sucrose and of the hydrates of sucrose is zero. The principal justification for these assumptions is that, in the case of cane sugar and chloral hydrate, they give results in agreement with those from the colligative properties.

Washburn<sup>3</sup> gives a very good review of hydration in solution, and notes that the colligative properties do not give mutually independent measures of the degree of hydration. The most rigorous treatment of either the

<sup>1</sup> H. C. Jones and F. H. Getman, *Am. Chem. J.*, 32, 327 (1904).

<sup>2</sup> H. L. Callendar, *Proc. Roy. Soc. (London)*, 80A, 466 (1900).

<sup>3</sup> E. W. Washburn, *Technology Quart.*, 21, 376 (1908).

<sup>4</sup> W. R. Bousefield, *J. Chem. Soc.*, 105, 600 (1914); *Trans. Faraday Soc.*, 13, 141-55 (1917).

<sup>5</sup> J. C. W. Frazer and R. T. Myrick, *THIS JOURNAL*, 38, 1907 (1916).

<sup>6</sup> A. W. Porter, *Trans. Faraday Soc.*, 13, 123 (1917).

<sup>7</sup> J. C. Philip, *J. Chem. Soc.*, 99, 711 (1907); *Trans. Faraday Soc.*, 3, 140-5 (1907).

<sup>8</sup> A. Einstein, *Ann. Phys.*, [4] 19, 301 (1906).

osmotic pressure or the freezing point is to calculate the activity of the water by thermodynamic formulas and calculate the degree of hydration by assuming that this activity is proportional to the molar fraction of the water. That is, it is assumed that the solution is semi-ideal as defined in the previous paper.<sup>9</sup> This is the method used by Callendar, by Washburn and by Frazer and Myrick. Jones and Getman and Bousefield use the simpler method of calculating the hydration from the variation of the freezing point from Raoult's formula, which really involves the above assumption and in addition that of infinite dilution.

The assumptions made by Bousefield and by Porter in their treatments of osmotic pressure are quite different, but they both arrive at the formula  $P(V-B) = RT$  as the exact one for osmotic pressure. Bousefield calculates the degree of hydration by taking  $V-B$  as the volume of free water, with its density the same as that of pure water. Porter takes  $B$  as the volume of the hydrate and assumes that the densities of the sugar and water in the hydrate are the same as those of the pure substances. When they both start from the same experimental results,<sup>10</sup> Bousefield's calculations range from 85 to 95% of Porter's. Possibly most of this difference is due to different approximations of experimental values. We will not analyze their assumptions in detail since the same formula can be obtained from a great many different assumptions, and most of them must be wrong because they are mutually exclusive. But they all need the fundamental assumption that the forces of attraction are independent of the concentration, the condition which we found sufficient for semi-ideal solutions.

The exact calculation of the activity from the osmotic pressure requires a knowledge of the densities and the compressibilities of the solutions; the calculation from the freezing point requires the latent heat of fusion of ice and its temperature variation. The results are so uncertain that Washburn, Callendar and Frazer and Myrick do not attempt to calculate the degree of hydration exactly, but they assign different integral values to the hydration and calculate the corresponding freezing point or osmotic pressure to determine which value for the hydration agrees best with the experimental results. Washburn found that the results of several observers on rather dilute solutions were fitted by the assumption of a hexahydrate. Callendar used the measurements of Jones and Getman on more concentrated solutions and found that a pentahydrate gave more satisfactory results. Frazer and Myrick studied a much larger concentration range and found that a hexahydrate gave best agreement for the dilute solutions, a pentahydrate for intermediate concentrations and a tetrahydrate for the most concentrated solutions.

<sup>9</sup> THIS JOURNAL, 43, 2390 (1921).

<sup>10</sup> Those of Morse and Frazer at 20°. *J. Chem. Soc.*, 105, 604 (1914); *Trans. Faraday Soc.*, 13, 129 (1917).

Vapor-pressure measurements have the advantage over the other colligative properties that they give the activity directly. They have the further advantage over the freezing point that they give results at constant temperature, and the effect of varying concentration can be determined directly. The accurate vapor-pressure measurements of Berkeley, Hartley and Burton<sup>11</sup> at 0° and 30° give us the most exact means of determining the hydration of sucrose. They are used in the calculations of this paper.

#### Analysis of Assumptions.

Since we are to attempt to determine the degree of hydration with considerably greater accuracy than has been done hitherto, it is necessary to examine our assumptions rather closely. If the activity of the water is proportional to its molar fraction, the polarity or thermodynamic environment of the solution must be independent of the concentration. This means that the forces of attraction acting on any molecule must be independent of the kind of molecules surrounding it. A water molecule must have the same forces exerted on it when it is entirely surrounded by other water molecules as when it is entirely surrounded by sugar molecules or as when it is surrounded by any mixture of the two. These mutual forces depend upon the fields of force surrounding the individual molecules.

The field of force of a sugar molecule ought to be similar to that of a water molecule, or rather to a string of water molecules. The carbon atoms must be nearly surrounded by the hydrogen atoms and hydroxyl groups, and the sugar molecule ought to be represented by a nearly uniform field of force due to the hydrogen and hydroxyl radicals in equal numbers. But these are, of course, the same groups as those of the water molecules, and the fields of force of a sugar molecule ought to be very similar to that of the water molecules which it displaces in solution. Although these forces are very much greater than those in organic liquids, if they are the same for sugar and for water, aqueous sugar solutions ought to obey the laws of semi-ideal solutions as accurately as do mixtures of two hydrocarbons. Certainly, carbohydrates ought to obey these laws much more closely than most other solutes, especially ionogens, which have quite different force fields. It seems that we are justified in assuming that all the variation from ideality is due to chemical action and that the molar fraction of the water is proportional to its activity.

We must next consider the ways in which the number of molecules of each substance in solution may change from the number added. The dissociation of both water and sugar may certainly be neglected. We will assume that any association of sugar may also be neglected; this is fairly well justified since the molar fraction of sugar is always less than 12%. Then there are but two kinds of chemical change possible: combination between two or more molecules of water, and between one of sugar and one or more of water. The extent of this latter reaction is what we are seeking to determine, and this makes it necessary to know the extent of the former. It is generally agreed that liquid water is partially associated into dihydrol ( $\text{H}_2\text{O}$ )<sub>2</sub> and perhaps a little trihydrol ( $\text{H}_2\text{O}$ )<sub>3</sub>, and various calculations have been made of the extent of association. It seems that these are generally high, and that most of the properties which are customarily taken as evidence for association can be more simply accounted for by the larger forces of attraction between the molecules. However, it is a surprising fact that the assumption as to the degree of association of the water makes very little difference in the determination of the degree of hydration of the sucrose. Washburn

<sup>11</sup> Earl of Berkeley, E. G. J. Hartley and C. V. Burton, *Phil. Trans.*, 218A, 295 (1919).



and Callendar assume that there is no association, Frazer and Myrick assume that all the water exists as dihydrol, and their conclusions are not very different.

We will make our calculations on two assumptions, which seem the limits of probability. First, we will assume that there is no association; second, that the association is approximately that calculated by van Laar<sup>12</sup> by the Ramsay-Ross Innes formula, 1.7 at 0° and 1.6 at 30° into dihydrol. That is, the molar fraction of monohydrol is 0.3 at 0° and 0.4 at 30°. The degree of association will not be the same in the sugar solutions as in pure water but will obey the law of mass action. Also, in the case of association, the molar fraction of water will not equal its activity relative to that of pure water as unity, but the activity must be multiplied by the molar fraction of monohydrol in pure water.

**Symbols.**—For convenience of reference the symbols used in this paper are collected and defined here. We will let subscripts *w*, 1, 2, *s*, *anh* and *hyd* refer to water, monohydrol, dihydrol, total sugar, anhydrous (unhydrated sugar) and hydrated sugar, respectively; *N* is the molar fraction existing in solution; *N'*, the molar fraction added; *N<sub>0</sub>*, the molar fraction of monohydrol in pure water; *a*, the activity; *a<sub>w</sub>*, the activity of monohydrol in terms of pure water as unity; *C*, the concentration of sucrose in grams per 100 g. of water; and *m* the number of molecules of water in one of sucrose hydrate.

**Derivation of Formulas.**—The calculation of the average degree of hydration is very simple for the case without association. From the number of grams of sugar added per 100 g. of water we calculate the number of moles of water added to one mole of sugar,

$$\frac{N'_w}{N'_s} = \frac{100 \times 342.24}{C \times 18.016} \quad (1)$$

The number of moles of water existing in solution for each mole of sucrose is the ratio of their molar fractions; and, since  $N_w + N_s = 1$ , then

$$\frac{N_w}{N_s} = \frac{N_w}{1 - N_w} = \frac{a_w}{1 - a_w} \quad (2)$$

The moles of water which disappear from solution for each mole of sucrose, or the average degree of hydration of the sucrose, is obtained by subtracting (2) from (1).

For the case with association there is a little greater complexity. From the laws of semi-ideal solutions we have directly,

$$N_1 = N_0 a_w. \quad (3)$$

If the association follows the law of mass action in molar fractions,

$$N_2 = K N_1^2 = K N_0^2 a_w^2 = (1 - N_0) a_w^2. \quad (4)$$

The replacement of  $K N_0^2$  by  $(1 - N_0)$  is arrived at by solving the equation for the special case of pure water, for which  $N_2 = 1 - N_0$  and  $a_w = 1$ . The molar fraction of the sugar is equal to  $1 - N_1 - N_2$ . The quantity of water, calculated as moles of monohydrol, existing in solution per mole of sugar will be:

$$\frac{N_1 + 2N_2}{N_s} = \frac{N_1 + 2N_2}{1 - N_1 - N_2} \quad (5)$$

The average degree of hydration is obtained by subtracting (5) from (1).

### The Measurements of Activity.

For these calculations it is desirable to have as many and as accurate measurements of the vapor pressure as possible. In a concluding note Berkeley remarks that the 30° values are slightly in error due to a small

<sup>12</sup> J. J. van Laar, *Z. physik. Chem.*, 31, 1 (1897).

temperature gradient in the apparatus, and he records a few measurements with one apparatus where this error was corrected. In order to get the best values for all concentrations, a study was made of the difference between these corrected results and the uncorrected ones for each apparatus. This included the measurements on  $\alpha$ -methyl glucose and sulfuric acid. It was found that the average correction in the quantity  $-\ln a_w$  was, within the experimental error, independent of the concentration and of the apparatus and equal to 0.00023. So this correction was added to all the uncorrected results, and the best value was taken as the average of these values with those of the note, each weighted proportionally to the number of observations which it represents. Table I gives the best illus-

TABLE I.  
VAPOR-PRESSURE CORRECTIONS AT 30°.

Conc. G. per 100 g. of H <sub>2</sub> O.	Main paper.	No. of Determ.	Note.	No. of Determ.	Best Value.
	$-\ln a_w$ +0.00023.		$-\ln a_w$		$-\ln a_w$ .
34.0	0.01927	5	0.01928	3	0.01927
56.5	0.03406	2		0	0.03406
81.2	0.05233	4	0.05239	1	0.05234
112.0	0.07739	3		0	0.07739
141.0	0.10282	2	0.10289	1	0.10284
183.0	0.14208	9	0.14206	2	0.14208
217.5	0.17563	1		0	0.17563

tration of the order of agreement. The measurements at 0° are not affected by this correction.

### The Average Degree of Hydration.

Table II gives the activity of the water and the degree of hydration of the sucrose calculated according to each of the two assumptions given above at 0° and at 30°. It will be noticed that the effect of the assumption of

TABLE II.  
ACTIVITY OF WATER AND AVERAGE DEGREE OF HYDRATION OF SUCROSE.

Conc.	$a_w$	0°.		$a_w$	30°.	
		Average hydrat. without assoc.	Average hydrat. with assoc.		Average hydrat. without assoc.	Average hydrat. with assoc.
34.0	.....	....	....	0.98092	4.46	4.83
56.5	0.96545	5.68	6.08	0.96651	4.76	5.13
81.2	0.94762	5.30	5.70	0.94901	4.78	5.15
112.0	0.92327	4.93	5.32	0.92553	4.53	4.89
141.0	0.89881	4.59	4.98	0.90227	4.24	4.59
183.0	0.86320	4.07	4.45	0.86755	3.83	4.17
217.5	0.83461	3.69	4.06	0.83893	3.53	3.86
243.0	0.81330	3.46	3.82	.....	....	....

association of the water is to increase the calculated value of the average hydration by about 4/10 of a molecule, and that the increase is nearly independent of the concentration and temperature. The average degree

of hydration decreases from about 6 to 3.5, and it is smaller at  $40^\circ$  than at  $0^\circ$  as might have been expected. This agrees with the conclusions of Frazer and Myrick from the osmotic pressure. The decreasing values for the more dilute solutions at  $30^\circ$  may be attributed to experimental error, for in the most dilute solutions an error corresponding to the correction made in Table I makes a difference of about 0.5 molecule in average hydration. This same explanation accounts for the results of Jones and Getman and of Porter on dilute solutions. Both find considerably larger values for dilute solutions; while Bousefield finds from the freezing-point measurements of Morse and Frazer that the values are irregular but always less than 6. This means that values of the average degree of hydration calculated for solutions more dilute than  $C=20$ , at least from any measurements yet recorded, are of little value.

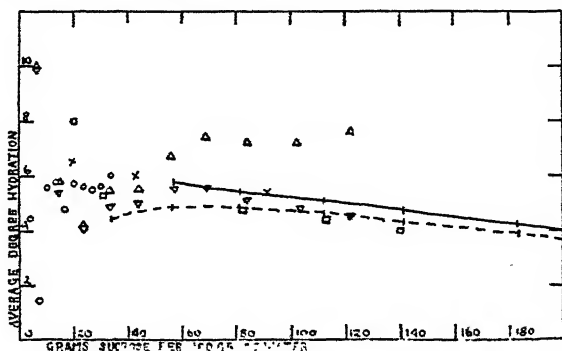


Fig. 1.—Average degree of hydration of sucrose.

#### SYMBOLS.

Full line: from vapor pressure at  $0^\circ$ , without association.

Dotted line: from vapor pressure at  $30^\circ$ , without association.

Triangles: from freezing point, Jones and Getman.

Inverted triangles: from freezing point, Jones and Getman, calculated by Scatchard.

Circles: from freezing point, Morse and Frazer, calculated by Bousefield.

Squares: from osmotic pressure at  $0^\circ$ , Berkeley, *et al.*, calculated by Porter.

Crosses: from solubility of hydrogen at  $18^\circ$ , calculated by Philip.

Fig. 1 contains some of the more interesting determinations of the average degree of hydration. The abscissas are concentrations (g. of sucrose per 100 g. of water), and the ordinates are the average degrees of hydration (molecules water for each molecule of sucrose). The values for the vapor-pressure determinations assuming association of the water are omitted as they give lines parallel to those assuming no association and would only

confuse the figure. Also, the figure does not extend to the most concentrated solutions for which the vapor pressures were measured. The increase of the hydration with increasing concentration found by Jones and Getman is seen to be due to the inaccuracy for concentrated solutions of their method of calculation. Their results as calculated by the author by the more accurate formula of Callendar<sup>13</sup> decrease regularly when they pass the concentration where the experimental error is very large. All the methods appear to agree within their respective experimental errors, which are not large for the concentrated solutions.<sup>14</sup>

### The Nature of the Hydrate.

We have already noted that the field of force of the sugar molecule is nearly uniform along its length. If there is a tendency for a water molecule to attach itself to one point in such a molecule, there should be a nearly

<sup>13</sup> Reference 2. p. 487, Formula VI.

<sup>14</sup> *Note added November 2.*—In the July number of *THIS JOURNAL* (43, 1391–6 (1921)), Kendall, comes to the very interesting and important conclusion that, for sufficiently dilute solutions, the degree of association of the water does not affect the vapor-pressure measurements, and that it may be neglected in calculating the degree of hydration of the solute from the colligative properties.

The present paper gives an interesting supplement to his conclusions in showing the magnitude of the effect for solutions which are not ordinarily considered as dilute. The weight-molar concentration varies from 1 *M* to 7 *M*. Since the calculations from the data on hand are relatively simple, the average degree of hydration was also calculated with the assumption that  $N_0 = 0.01$  and 0.001, that is that in pure water only one molecule in every hundred and in every thousand, respectively, is monohydrol, while the others are dihydrol. The two calculations agree within 0.01 molecule in every case, so that only those for  $N_0 = 0.001$  are tabulated. The differences between these values and those for  $N_0 = 1.0$ , or for no association, (from Table II) are also given.

TABLE II A.  
AVERAGE DEGREE OF HYDRATION OF SUCROSE, ASSUMING  $N_0 = 0.001$ .

Conc.	Av. hydrat.	0°.		30°.	
		Diff. from no. Assoc.		Av. hydrat.	Diff. from no. Assoc.
34.0	....	....		4.97	0.51
56.5	6.17	0.49		5.25	0.49
81.2	5.79	0.49		5.27	0.49
112.0	5.41	0.48		5.01	0.48
141.0	5.06	0.47		4.71	0.47
183.0	4.53	0.46		4.29	0.46
217.5	4.14	0.45		3.98	0.45
243.0	3.91	0.45		....	....

In this concentration range, these widely different assumptions make a difference of approximately one-half molecule in the average hydration. Comparison with Fig. 1 will indicate the unimportance of this compared to the experimental error in dilute solutions. Whether this factor need be considered in any case depends, of course, upon the accuracy of the results desired and justified by the experimental accuracy and the validity of the laws of semi-ideality for the case in question.

equal tendency toward attachment at several other points. Probably the addition of a water molecule at one point will not change the field or tendency to hydrate at other points. Then that hydrate in which all the equivalent positions are filled ought to be very much more stable than any of the lower hydrates. This hydrate will also have a nearly uniform field and may have a tendency to hydrate further. If so there will be another higher hydrate, existing in smaller quantities than the first, but larger than any of the other hydrates.

We will assume that there is one such hydrate of so great a relative stability that the quantities of all the other hydrates are negligibly small, and that the whole system can be considered as an equilibrium between water, anhydrous sugar and this hydrate. If the solution is semi-ideal the formation of this hydrate will obey the law of mass action in terms of molar fractions. By application of the law we can determine how well the assumption of any hydrate will explain the experimental facts.

It must be emphasized that this theory of one rather complex hydrate is not applied to hydration in solution in general, but is limited to carbohydrates, whose large uniform molecules should give them very special properties. This explanation of a varying average degree of hydration is believed to be original; and, although the literature contains many statements that hydrate formation obeys the law of mass action, there seems to have been no previous attempt to test with the experimental results.

Consider first the case in which the water is not associated. The law of mass action for the reaction  $C_{12}H_{22}O_{11} + mH_2O \rightleftharpoons C_{12}H_{22}O_{11} \cdot mH_2O$  will be

$$\frac{N_{hyd}}{N_{anh} \times (N_w)^m} = K_m. \quad (6)$$

We know  $N_w/N_s$  and the average degree of hydration. Since  $N_w + N_s = 1$ ,

$$1 + \frac{N_w}{N_s} = \frac{1}{N_s}.$$

The average degree of hydration divided by  $m$  will be

$$\frac{N_{hyd}}{N_s}, \text{ and } 1 - \frac{N_{hyd}}{N_s} = \frac{N_{anh}}{N_s}.$$

From these ratios the calculation of the molar fractions and of  $K$  is direct and simple.

For the case in which the water is associated, we have already determined  $N_1$ , which must replace  $N_w$  in the formula, and  $N_s$  in calculating the average degree of hydration. Dividing this average degree of hydration by  $m$  and multiplying by  $N_s$  will give  $N_{hyd}$ , and  $N_{anh} = N_s - N_{hyd}$ . This gives us all the data necessary for calculating  $K_m$  by Equation 6. Table III contains the values of  $K$  for  $m=6$  and  $m=7$ . The choice must lie between these two, for the values of  $K_s$  decrease too rapidly to be possible

TABLE III.  
EQUILIBRIUM CONSTANTS FOR HYDRATION OF SUCROSE.  
Without association.

Conc.	0°.		30°.		With association.		30°	
	$K_6$	$K_7$	$K_6$	$K_7$		$K_6$	$K_7$	$K_7$
34.0	....	....	3.25	2.01	....	....	1.14	1.56
56.5	21.76	5.49	4.72	2.70	absurd	38.76	1.76	2.12
81.2	10.52	4.56	5.38	3.11	36.22	29.28	2.02	2.45
112.0	7.42	4.16	4.92	3.16	17.35	25.33	1.71	2.43
141.0	6.18	4.02	4.47	3.16	12.66	23.74	1.48	2.39
183.0	5.10	3.89	4.14	3.27	9.50	22.32	1.31	2.44
217.5	4.72	3.95	4.09	3.47	8.48	22.35	1.26	2.57
243.0	4.71	4.16	....	....	8.33	23.39	....	....

and  $K_6$  leads to absurd results. The values of  $K_6$  are very good for the most concentrated solutions, but they increase rapidly with dilution for the more dilute; the values for  $K_7$  are fair throughout. At 30° either gives good constancy. The results for the dilute solutions are much less important, for there a small error in the vapor pressure corresponds to a large change in  $K$ . To illustrate this and to give a better test of the agreement of the theory with experiment, calculations are given in Table IV of the values of the vapor pressure which give constant values of  $K$  for the case without association.

These calculations have to be made by trial and error and are rather tedious. The values selected for the constants are approximately those which give the smallest deviations from the experimental results, but the choice may be more fortunate in one case than in another. So the results for  $K_6$  and  $K_7$  must not be compared too closely. At 0°, however, the heptahydrate clearly gives much better agreement. The table shows the enormous effect in  $K$  of a small error in the vapor-pressure measurements for the dilute solutions.

TABLE IV.  
VALUES OF VAPOR PRESSURE WHICH GIVE CONSTANT VALUES FOR  $K$  (WATER NOT ASSOCIATED).

Conc.	0°.		30°.	
	$K_7=4.815$ $a_w$ calc.	dev.	$K_7=4.00$ $a_w$ calc.	dev.
34.0	0.98083	-0.00009	0.98064	-0.00028
56.5	0.96649	+0.00104	0.96589	+0.00044
81.2	0.94930	+0.00168	0.94808	+0.00046
112.0	0.92565	+0.00238	0.92359	+0.00032
141.0	0.90145	+0.00264	0.89888	+0.00007
183.0	0.86441	+0.00121	0.86251	-0.00069
217.5	0.83399	-0.00062	0.83415	-0.00046
243.0	0.81250	-0.00080	0.81482	+0.00152

### The Activity of the Sucrose.

It is possible to attack the constitution of the hydrate from another

point of view. By the use of Lewis and Randall's modification<sup>15</sup> of the Duhem-Margules equation for the dependence of the activity of one component upon that of the other, it is possible to calculate the change in the activity of the sucrose with changing concentration. The method of calculation is to plot  $\log(a_w/N'_w)$  against  $N'_w/N'_{anh}$  (abscissa) and to measure the area under the curve between the concentrations chosen. This gives the change in  $\log(a_{anh}/N'_{anh})$  for it is the anhydrous sugar which is added to the solution. If our theory is correct  $a_{anh}/N'_{anh} = N_{anh}/N'_{anh}$ . With solutions of such strength as we are using it is unsafe to extrapolate in either direction. The simplest method is to make the comparison directly between the change in  $\log(a_{anh}/N'_{anh})$  and that in  $\log(N_{anh}/N'_{anh})$  as calculated according to the various assumptions. Since the values of the latter quantity are more accurate for the higher concentrations, the change is calculated from the highest concentration.

Table V gives the values of  $N'_w/N'_{anh}$ ,  $\log(a_w/N'_w)$  and the increase of  $\log(a_{anh}/N'_{anh})$  at 0° and at 30°. Table VI gives the values of the change in  $\log(N_{anh}/N'_{anh})$  as calculated according to the different assumptions and the differences between these values and the observed

TABLE V.  
ACTIVITY OF SUCROSE BY DUHEM-MARGULES EQUATION.  
0°. 30°.

Conc.	$\frac{N'_w}{N'_{anh}}$	$\log \frac{a_w}{N'_w}$	$\Delta \log \frac{a_{anh}}{N'_{anh}}$	$\log \frac{a_w}{N'_w}$	$\Delta \log \frac{a_{anh}}{N'_{anh}}$
34.0	55.872	.....	.....	-0.00066	-0.4520
56.5	33.622	-0.00254	-0.4679	0.00206	0.3914
81.2	23.395	0.00519	0.3946	0.00456	0.3237
112.0	16.961	0.00979	0.3035	0.00873	0.2402
141.0	13.473	0.01524	0.2218	0.01357	0.1668
183.0	10.381	0.02394	0.1198	0.02176	0.0705
217.5	8.734	0.03144	0.0494	0.02920	0.0000
243.0	7.818	0.03747	0.0000	.....	.....

TABLE VI A.  
COMPARISON OF ACTIVITY AND MOLAR FRACTION OF SUCROSE. (WITHOUT ASSOCIATION).  
0°. 30°.

Hexahydrate.				Heptahydrate.			
$\Delta \log \frac{N_{anh}}{N'_{anh}}$		Diff.		$\Delta \log \frac{N_{anh}}{N'_{anh}}$		Diff.	
34.0	.....	.....	.....	-0.3661	-0.0859	-0.2961	-0.1559
56.5	-1.0352	+0.5673	.....	0.4319	+0.0405	0.3221	-0.0693
81.2	0.6720	+0.2774	.....	0.4088	+0.0851	0.2957	-0.0280
112.0	0.4515	+0.1480	.....	0.2960	+0.0558	0.2178	-0.0224
141.0	0.3064	+0.0846	.....	0.1929	+0.0261	0.1448	-0.0220
183.0	0.1435	+0.0237	.....	0.0743	+0.0038	0.0571	-0.0134
217.5	0.0501	+0.0007	.....	0.0000	.....	0.0000	.....
243.0	0.0000	.....	.....	0.0000	.....	0.0000	.....

<sup>15</sup> G. N. Lewis and M. Randall, THIS JOURNAL, 43, 233 (1921).

TABLE VI B.  
 (WITH ASSOCIATION.)

34.0	.....	.....	.....	-0.3990	-0.0530	-0.2968	-0.1552
56.5	.....	.....	-0.6493	+0.1814	0.4992	+0.1078	0.3340
81.2	-0.9480	+0.5534	0.4734	+0.0788	0.4816	+0.1579	0.3109
112.0	0.5621	+0.2586	0.3331	+0.0296	0.3396	+0.0994	0.2269
141.0	0.3624	+0.1406	0.2304	+0.0086	0.2152	+0.0484	0.1489
183.0	0.1614	+0.0416	0.1096	-0.0102	0.0806	+0.0101	0.0575
217.5	0.0549	+0.0055	0.0387	-0.0107	0.0000	.....	0.0000
243.0	0.0000	.....	0.0000	.....	.....	.....	.....

changes in  $\log(a_{\text{anh}}/N'_{\text{anh}})$ . Again the values for the more concentrated solutions agree better for the hexahydrate, while over the greater part of the range they fit the heptahydrate better. And again, for the more concentrated solutions, there is a variation in the opposite direction for these two hydrates, showing that higher or lower hydrates would give poorer agreement.

These results are important as showing that the activity of the sucrose varies approximately as it should if our theories are correct. They confirm the idea that a varying proportion of the sugar exists in the unhydrated condition. As a test between the different assumptions, however, they are not entirely independent of the calculations of the equilibrium constants. If we use the vapor pressures which give constant values of  $K_s$ , the variation in  $\log(a_{\text{anh}}/N'_{\text{anh}})$  will agree exactly with that of  $\log N_{\text{anh}}/N'_{\text{anh}}$ , and similarly for the heptahydrate.

### Interpretation of the Results.

The vapor-pressure measurements do not agree within their apparent experimental error with the existence of either a hexahydrate or a heptahydrate alone, and our results seem to indicate that no assumption concerning the association of the water will better the agreement. It is possible that there is a constant experimental error in the vapor-pressure measurements which is larger than the agreement of the individual experiments indicates. An error of 0.1% at 30° and of 0.2–0.3% at 0° would account for the variation either for the hexahydrate or for the heptahydrate, depending upon the direction of the deviation. This is, however, from 5 to 10 times the apparent experimental error.

There seem to be three other possible explanations. First, our solutions may not be strictly semi-ideal, and the deviation from proportionality between the activities and the molar fractions might explain the results for either the hexahydrate or the heptahydrate, depending again upon the direction of the deviation. Second, our assumption of one hydrate so much more stable than the others may be entirely wrong, and the solution may contain an equilibrium mixture of a large number of hydrates in nearly equal quantities. Third, our assumption of one hydrate may be



only slightly in error, and there may be but one higher hydrate as suggested earlier in this paper. If so the predominating hydrate must be the hexahydrate or possibly an even lower one. If a hexahydrate, the agreement of the concentrated solutions would be due to the fact that the second hydrate would exist only in very small quantities in these solutions. The increasing quantities on dilution would account for the increase of  $K$  when calculated for the hexahydrate alone. Doubtless, given an arbitrary choice of the composition of this hydrate and its constant of dissociation, it would be possible to fit the experimental results within their error of measurement. But the formula would involve four arbitrary constants, and its agreement would not give a very strong confirmation of the theory. At  $30^\circ$  this higher hydrate would exist in much smaller quantities than at  $0^\circ$ .

**Evidence from other Sources.**—The surest proof of the existence of a compound in solution is its separation as a solid phase, identified by analysis or by the freezing-point curve. Guthrie<sup>16</sup> mentions a cryohydrate separating at  $-8.5^\circ$  with a composition of 5.27 mole per cent. (51.4%) sugar. This is far off the curve for anhydrous sugar and, if it were real, would indicate a hydrate. However, the ice curve drawn from Guthrie's other measurements will not pass through this point without sharp curvature. Jones and Getman obtained a smooth curve up to a concentration of 6.43 mole per cent. which freezes at  $-9.13^\circ$ . The author has made preliminary measurements extending to 8 mole per cent. where the freezing point is about  $-13^\circ$ . This extends the ice curve slightly beyond the sugar-solubility curve. In no case did anything but ice separate and the curve seems entirely regular. The fact that only ice separated in these experiments does not prove, of course, that the system ice: solution is not a metastable one from which a hydrate might be separated. The study of the freezing-point curve will be continued, and will at least extend the ice curve to meet that of sugar. So the present evidence from the phase rule means nothing. The molar fraction of the hydrate is small even at its highest concentration, and it should be so similar in polarity to the other components of the solution that it ought to be quite soluble. Then failure to isolate a solid hydrate would not be unexpected.

All of the physical properties of sucrose solution which have been measured seem to obey the additive law so closely that they give no indication except that there is a slight variation from ideality, but not necessarily from semi-ideality.

If the degree of association of water were accurately fixed, some insight could probably be gained from the heat of dilution of sucrose solutions. But the heat of reaction calculated from the change in the equilibrium constant with the temperature would depend very largely upon the assumption as to the degree of ionization of the water. There would also

<sup>16</sup> F. Guthrie, *Phil. Mag.*, [5] 2, 216 (1876).

be the accompanying reaction of the association of the water with a large thermal effect.

The only evidence other than that from the colligative properties seems to be that from the speed of inversion. It has been shown in the preceding paper that probably 6, but possibly 5 or 7 water molecules enter into the reaction with each sugar molecule, and that the most probable explanation is a preliminary hydration of the sugar molecule. The assumptions underlying the speed of inversion method are almost entirely different from those of the present paper. It is true that the assumption of semi-ideal solution was made in changing from activity of sucrose to molar fraction. Also the justifiability of that assumption is confirmed by its success in accounting for the variation of hydrogen-ion activity on the addition of sugar. Our only other assumptions, except for small correcting terms which might have been neglected, are that the speed of reaction in solutions is proportional to the activities of the reactants, and that the activity of the hydrogen ion which determines its catalytic effect is the same as that which determines the electromotive-force measurements.

The determination from the vapor pressures assumes that the solutions are semi-ideal, and that there is one hydrate which is very much more stable than the others. The hypothesis that the formation of the hydrate obeys the law of mass action in terms of molar fractions follows as a thermodynamic necessity from the assumption of semi-ideality. We have two independent methods which lead us to the conclusion that aqueous sugar solutions are equilibrium mixtures of sucrose, water and a hydrate of sucrose containing probably 6 molecules of water. There appears to be no evidence which contradicts this conclusion.

### Summary.

1. The average degree of hydration of sucrose in water solution at  $0^{\circ}$  and at  $30^{\circ}$  is calculated from the vapor pressures.
2. The theory is advanced that sucrose solutions are equilibrium mixtures of water, unhydrated sucrose and a single hydrate, and that the relative quantities of these substances are determined by the law of mass action.
3. This theory is tested by comparison of the experimental results with those calculated from the law of mass action. The agreement is fair for either a hexahydrate or a heptahydrate. The theory is also tested by a comparison of the activity of the sucrose calculated from its degree of hydration and that calculated by the Duhem-Margules equation. The results confirm those obtained by use of the law of mass action method.
4. The results agree with those obtained from the inversion of sucrose in the preceding paper.

## NOTE.

**The Precipitation of Arsenic Sulfide from Arsenates.**—The precipitation of arsenic sulfide from acid solutions of arsenates by hydrogen sulfide may be greatly hastened by the presence of a soluble iodide. This catalytic effect is doubtless due to the reduction of the arsenic acid to arsenious acid by the hydriodic acid, the iodine being continuously reconverted to hydriodic acid by the hydrogen sulfide.



The arsenious acid yields arsenic trisulfide readily, particularly in the presence of free hydrochloric acid. The assumed reduction of the arsenate to arsenite is confirmed by analysis of the precipitate, which is found to be mainly arsenic trisulfide and sulfur, with varying amounts of the pentasulfide.

This has been applied in the work in qualitative analysis at the University of Illinois in the following way. Just before passing in the hydrogen sulfide, 1 or 2 cc. of 1.0 *N* ammonium iodide solution (potassium or sodium iodide would vitiate subsequent tests for these cations) is added to the hot solution, which contains 4 cc. of 6 *N* hydrochloric acid in a volume of 40 cc. Precipitation begins immediately, and is usually complete in 4 or 5 minutes, depending on concentrations, temperature, agitation and so forth. Not only is the time for complete precipitation of pentavalent arsenic shortened to approximately  $\frac{1}{3}$  of that usually required, but the chances are much lessened that the student will fail to detect arsenic because of non-precipitation at this point.

Apparent complications arise in the precipitation of mercury and copper as iodides and in the partial reduction of the former to the mercurous state. However, these effects are rectified during the digestion with ammonium polysulfide, which oxidizes both metals to the higher valence, precipitating them as mercuric and cupric sulfides.

CHEMISTRY DEPARTMENT OF THE  
UNIVERSITY OF ILLINOIS.  
URBANA, ILLINOIS.  
Received July 22, 1921.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OREGON.]

LABORATORY PREPARATION OF ACETALDEHYDE.<sup>1</sup>

BY CHESTER E. ADAMS WITH ROGER J. WILLIAMS.

Received July 7, 1921.

None of the laboratory methods for the preparation of acetaldehyde by the oxidation of alcohol is highly satisfactory, as the yields are low and uncertain. Gattermann's method<sup>2</sup> is recommended by Beilstein but the yield of aldehyde-ammonia at best is only about 23% of the calculated. In ordinary practice the yields are considerably lower than this. Noyes<sup>3</sup> predicts a yield of about 15% for the method outlined.

Preliminary work proved the unsatisfactoriness of the methods. If the oxidizing mixture used oxidizes the aldehyde more readily than alcohol (found by experiment to be true) then the production of aldehyde even in small amounts must be due to its low boiling point and its ability to escape from the mixture before oxidation takes place.

With this idea as a working basis several methods were used to increase the volatilization of the aldehyde, and the use of a mechanical stirrer was the only method found practicable. By this means yields were obtained more than double any obtained previously. That the stirring was responsible for the increase was proved by using the same procedure and apparatus except that the stirring was omitted, in which case the yield was very low.

Working with essentially the same apparatus and method, different concentrations of oxidizing agent were then tried to determine whether under these conditions better results could be obtained with some other concentration than that recommended by Gattermann.

The figures show that the amount of sodium dichromate recommended by Gattermann (200 g. per 100 g. of alcohol) could not be materially im-

TABLE I.  
EXPERIMENTAL RESULTS.

	Alcohol used (95%). G.	Sodium dichro- mate used per 100 g. alcohol. G.	Additional dichromate on reaction flask at the start. G.	Aldehyde am- monia obtained. G.	Yield. %.
1.....	50	200	0	27	43
2.....	37	200	0	21	45
3.....	45	190	0	23	40
4.....	47	190	0	25	42
5.....	33	170	0	17	41
6.....	58	170	0	30	41
7.....	37	200	25	14	30
8.....	38	200	100	9	19

<sup>1</sup> The material of this paper was submitted by Chester E. Adams in partial fulfilment of the requirements for the degree of Master of Science at the University of Oregon.

<sup>2</sup> Gattermann, "Practical Methods of Organic Chemistry," 1915, p. 167.

<sup>3</sup> Noyes, "Organic Chemistry for the Laboratory," 1911, p. 89.

proved upon. Not only are the yields much better than those obtainable formerly, but practically the same results can be obtained repeatedly by using the method. The amounts of alcohol varied in the different experiments because it was forced into the reaction flask by air pressure through a capillary tube and the amount used was determined by difference. The capillary tube was found a convenient means of introducing the alcohol in a steady stream, but a dropping funnel can be used successfully. The method which proved most successful is outlined below.

### Method.

A 1-liter flask is fitted with a 3-holed stopper carrying a reflux condenser tube of good length and placed at an angle for refluxing, a dropping funnel (or capillary tube through which liquid can be forced), and an electrically-driven stirrer provided with a mercury seal. The mercury seal is used to prevent loss of aldehyde through the opening, and in our experiments was of the same type as the water seal recommended by Fischer for a similar purpose.<sup>4</sup> Through the condenser is passed a current of water at about 25°. The upper end of the condenser is fitted with a delivery tube of good size dipping into a small wide-mouthed flask containing about 80 cc. of well-dried ether. This flask is in turn connected with a second similar flask containing about 30 cc. of ether to absorb any aldehyde passing over. One hundred and ten g. of conc. sulfuric acid in 200 cc. of water is put into the flask and the stirrer adjusted. The solution is then heated to about the boiling point. A mixture of 50 g. of alcohol (95%) 100 g. of sodium dichromate and 100 cc. of water is then introduced slowly through the capillary or the dropping funnel, with mechanical stirring. With a small flame under the flask the alcohol is admitted as fast as allowed by complete absorption in the ether and sufficient cooling in the condenser. When the alcohol is all admitted the reaction mixture is stirred for a few minutes as long as aldehyde appears to come over. The ether solution is then saturated with dry ammonia in the usual way and allowed to stand overnight when the crystals of aldehyde-ammonia are filtered off, pressed dry, freed from remaining ether and weighed. For the preparation of purer aldehyde-ammonia probably a preliminary distillation such as recommended by Gattermann should be made before the aldehyde is collected in the ether.

### Summary.

A study of the oxidation of alcohol to aldehyde by sodium dichromate showed that the introduction of a mechanical stirrer to disengage the aldehyde as fast as it is formed, increases the yield of aldehyde-ammonia at least 100% and gives consistent results. The method used is outlined.

EUGENE, OREGON.

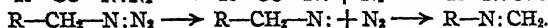
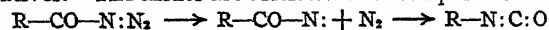
<sup>4</sup> Fischer, "Preparation of Organic Compounds," 1917, p. 41.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]  
 REARRANGEMENTS OF SOME NEW HYDROXAMIC ACIDS RE-  
 LATED TO HETEROCYCLIC ACIDS AND TO DIPHENYL- AND  
 TRIPHENYL-ACETIC ACIDS.<sup>1</sup>

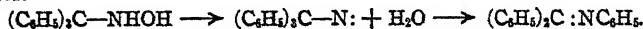
By LAUDER W. JONES AND CHARLES D. HURD.

Received July 11, 1921.

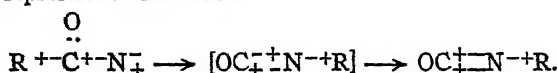
A summary of the serious attempts to explain the mechanism of the Beckmann rearrangement must necessarily include the work of Hoogewerff and van Dorp,<sup>2</sup> Hantzsch,<sup>3</sup> Stieglitz,<sup>4</sup> and Jones.<sup>5,6</sup> The types of compounds generally assumed to undergo this rearrangement are the azides, mono-substituted  $\beta$ -hydroxylamines, monobromo-amines, oximes, amidoximes, oximido acid esters, acid halogen amides and the hydroxamic-acid derivatives. The azides are assumed to decompose as follows:



These two cases, together with the mono-substituted  $\beta$ -hydroxylamines presented below, furnish examples of the Beckmann rearrangement that have never been explained successfully except by the theory of Stieglitz and of Jones.



Stieglitz was the first investigator to propose the hypothesis that univalent nitrogen derivatives form the primary decomposition products in these rearrangements. His extensive experimental work has demonstrated the soundness of this postulate.<sup>7</sup> Some years later, Jones formulated the reaction mechanism in a detailed manner by applying the theory of electron valence to the interpretation given by Stieglitz. The electron mechanism was represented as follows.<sup>5,6</sup>



Unless there were a driving force acting to cause the transfer of the radical from carbon to nitrogen, it would still be difficult to imagine why the

<sup>1</sup> This paper incorporates a thesis presented by Charles D. Hurd in 1921 to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1887); **8**, 173 (1889).

<sup>3</sup> Hantzsch, *Ber.*, **35**, 228, 3579 (1902); *ibid.*, **27**, 1256 (1894).

<sup>4</sup> Stieglitz, *Am. Chem. J.*, **18**, 75 (1896); **29**, 49 (1903); Stieglitz and Earle, **30**, 399, 412 (1903); Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914); etc.

<sup>5</sup> Jones, *Am. Chem. J.*, **43**, 1 (1912); **50**, 414 (1913).

<sup>6</sup> *THIS JOURNAL*, **36**, 1288 (1914); etc.

<sup>7</sup> The rearrangement of ketoximes, which was originally attributed by Stieglitz to the formation of univalent nitrogen derivatives, is now regarded as an exception. His present view assumes "the rearranging power of an intermediate hydrochloride of a univalent nitrogen derivative, acting in place of the ordinary free univalent nitrogen compound." See Montagne (*Ber.*, **43**, 2015 (1910)), Schroeter (*ibid.*, **44**, 1207 (1911)), and Stieglitz.

reaction should proceed, even with the explanation offered. Such a driving force is to be found in the shifting of electrons within the molecule. Jones stressed particularly that the free valences of univalent nitrogen afforded the "stage setting required to furnish a suitable environment in which the essential action," *viz.*, the transfer of the radical from carbon to nitrogen might take place. In a footnote to an article published some months later,<sup>4</sup> Stieglitz stated that, in regard to the most fundamental questions of these rearrangements "postulating a shifting of electrons from carbon to nitrogen, and a migration of a positive radical, Professor Jones and the writer are happily in entire agreement."

As viewed from present day standards, this interpretation with very slight modifications, still holds. In late years, worthy evidence<sup>5</sup> has been submitted to show that the positive charges possessed by an atom are centered in its nucleus. In compounds which are formed by the sharing of negative electrons, a "bond" consists of a pair of electrons held in common between two atoms. This theory of a chemical bond requires symbols in which positive charges cease to appear, except as they form an integral part of the nucleus of any atom. Such an interpretation would mean simply that a symbol,  $C^+ \vdash N$ , employed at a time when ion charges, rather than electrons in the present sense, held the attention of chemists, would now become  $C : N$ ; that is, the carbon atom and the nitrogen atom share a single pair of electrons. This conception of paired electrons would account just as readily for the driving force necessary to bring about rearrangement. Thus, the system of symbols  $C : N \rightarrow C \vdash N$  is equivalent to  $C^+ \vdash N \rightarrow C \vdash N$  previously employed.

Possibly the formula  $C \vdash N$  contains an assumption not necessarily implied by the formula  $C : N$  in which two pairs of electrons are shared, since the former suggests that a compound which contains such a group would not be exactly non-polar, although it should not be regarded as polar in the sense in which  $Na^+ Cl^-$  must be. To meet difficulties of this kind, Lewis employs formulas in which the pairs of electrons are placed nearer one symbol than another, *e. g.*,  $A : B$ , which implies that the molecule  $AB$  shows some polar characteristics. With these modifications to adapt the old electronic formulas to present day practices, equations may be given to represent the rearrangement of a univalent nitrogen derivative of a hydroxamic acid.

Formulas I, Ia and Ib represent the intermediate univalent nitrogen derivative; Formulas II, IIa and IIb represent a transition stage, the rearrangement of the positive radical, R. It will be noted that, in Formula II, although the carbon atom still has its "octet" completed, the nitrogen atom has only 6 electrons in the outer shell. By the sharing of electrons, both the nitrogen and the carbon atoms may complete their octets. This

<sup>5</sup> G. N. Lewis, Langmuir and others.

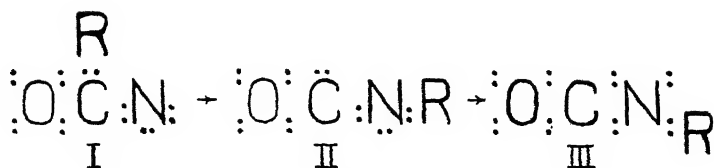


Fig. 1.

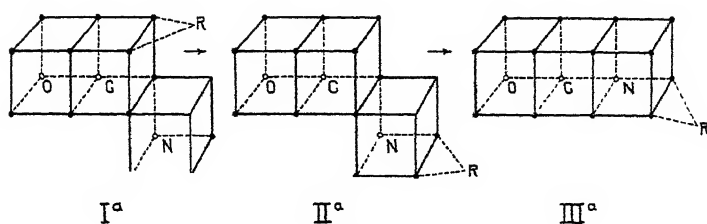
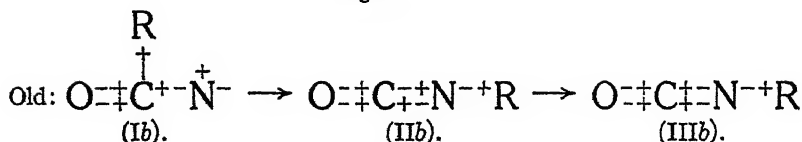


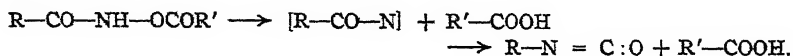
Fig. 2.



is represented in Formulas III, IIIa and IIIb, the isocyanate stage in the rearrangement.

With this conception, it is easy to understand why the radical R is able to part company with carbon and attach itself to nitrogen. No hypothesis has been offered, however, to explain why one radical R will do so with much greater readiness than some other radical R'. To seek an explanation of this factor was one of the motives that prompted the work which follows.

Chief interest in the present paper centers upon the reactions of dihydroxamic acids. They have been shown to rearrange in the following manner.

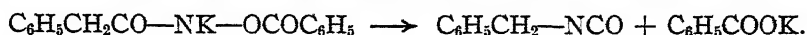


Either the action of heat, or of warm solutions of alkalis, will produce this effect. In the former case, the isocyanate is formed by dry distillation of the dihydroxamic acid, or, preferably, by heating a salt of the acid. Usually there is a fairly definite temperature at which the decomposition of the dry salt takes place. However, certain cases have proved that it is not a reliable method to use when two similar compounds are to be judged for comparative ease of rearrangement. If solutions are employed, the isocyanate generally reacts immediately with water to form the amine, or the corresponding disubstituted urea. The behavior of neutral solutions



of the sodium or of the potassium salts in water seems now to furnish a more accurate criterion by which to judge the ease of rearrangement of these particular compounds

A few years ago, phenyl-acethydroxamic acid<sup>9</sup> was studied. The benzoyl ester of this acid was capable of forming salts which possessed unusual instability towards heat. Its solid potassium salt suffered Beckmann rearrangement spontaneously at room temperature. Here,



Because of this rearrangement, it was not found possible to form a clear solution of the salt in water, unless it was prepared immediately after the isolation of the salt. We have recently repeated this experiment, and found, in addition, that the clear solution, when left at room temperature for 2 hours, did not undergo a noticeable rearrangement. A small white precipitate of the urea collected in 10 hours, however. The similar potassium salt of the benzoyl ester of acethydroxamic acid,  $\text{CH}_3-\text{CO}-\text{NK}-\text{OCOC}_6\text{H}_5$ , did not possess this marked tendency to rearrange; so the replacement of hydrogen by phenyl must have occasioned the decrease in stability. With this in view, diphenyl- and triphenyl-acethydroxamic acid were deemed important compounds to study. The sodium or the potassium salts of their acyl esters should exhibit a greater capacity for rearrangement in solution than the similar compounds in the monophenyl series.

The univalent nitrogen compounds,  $[\text{R}-\text{CO}-\text{N}]$ , which have been assumed to be the primary products of decomposition, have never been isolated. The isocyanates, resulting from rearrangements which involve readjustments of electrons, are obtained instead. It was not our object in this investigation to try to isolate such derivatives. Indeed, with the groupings  $[(\text{C}_6\text{H}_5)_2\text{CH}-\text{CO}-\text{N}]$ , and  $[(\text{C}_6\text{H}_5)_3\text{C}-\text{CO}-\text{N}]$  the tendency to rearrange to form isocyanates should be greater than in any case previously studied.

Triphenylmethyl is a group that is known to display a tendency to exist as a free radical. Certainly, then, it would seem highly probable that a derivative such as  $[(\text{C}_6\text{H}_5)_3\text{C}-\text{CO}-\text{N}]$ , would be far more apt to separate momentarily into  $[(\text{C}_6\text{H}_5)_3\text{C}-]$  and  $[-\text{CO}-\text{N}]$  than a group such as  $[\text{H}_3\text{C}-\text{CO}-\text{N}]$  in which the linking of carbon to carbon is conceived to be stronger. The latter would give rise to  $[\text{H}_3\text{C}-]$  and  $[-\text{CO}-\text{N}]$ . By no means must it be considered probable that free radicals displaying the great order of reactivity shown by triphenylmethyl could ever be isolated while in the presence of the highly reactive univalent nitrogen.

As a result of earlier experiments, and of those included in this article,

<sup>9</sup> Thiele and Pickard, *Ann.*, 309, 189 (1899); Jones, *Am. Chem. J.*, 43, 6 (1912).

we were led to formulate an hypothesis which may be stated as follows: the relative ease of rearrangements of the Beckmann type is dependent upon the tendency for the radical R, in the univalent nitrogen derivative, *e. g.*, [R—CO—N], to exist as a free radical.

It must be noted that this hypothesis does not deal with the ease of formation of the univalent nitrogen compound. It is essential that the group —NHX in the original molecules, R—CO—NHX, be identical when two different compounds are compared. An extreme case of the effect produced when different groups are substituted is displayed in the acyl alkyl halogen amines, *e. g.*, R—CO—NCl—C<sub>6</sub>H<sub>11</sub>. Stieglitz observed that compounds of this type show no tendency to undergo rearrangement.<sup>10</sup>

Triphenylmethyl, and other groups that are known to exist free, have been shown to exhibit polar characteristics in many of their compounds. For example, triphenylmethyl bromide displays marked conductivity when dissolved in sulfur dioxide;<sup>11</sup> this is one of the arguments which leads to the belief that an ion, or a pseudo-ion, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C<sup>+</sup>, must exist in the solution. Furthermore, it has been shown that triphenylmethyl is formed in the cathode chamber when triphenylmethyl bromide is electrolyzed. In fact, appropriate solutions of triphenylmethyl, itself, conduct the electric current.<sup>12</sup> These are important facts in support of our hypothesis.

From the standpoint of our hypothesis, it would seem that the tendency for the phenylmethyl radical, C<sub>6</sub>H<sub>5</sub>—CH<sub>2</sub>, to exist free is greater than for methyl, CH<sub>3</sub>. The allusion is to the experimental fact that the derivatives of phenyl-acethydroxamic acid suffer rearrangement more easily than those of acethydroxamic acid. On the basis of this hypothesis, also, the observation made by McCoy and Stieglitz,<sup>13</sup> and supplemented by van Dam,<sup>14</sup> that dibromo-salicylic-bromo-amide rearranges even at —12°, is evidence for the tendency of the radical C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>.OH to exist free. Other bromo-amides that have been studied exhibit a more stable character.

From this same standpoint, it may be predicted that any substituted acethydroxamic acid containing a tri-aryl methyl group will undergo rearrangement with great ease. For example, tri-bisphenyl-acethydroxamic acid, (C<sub>6</sub>H<sub>5</sub>—C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C—CO—NHOH, should form derivatives that are even more unstable than triphenyl-acethydroxamic acid. The group tribisphenylmethyl, in contrast to triphenylmethyl, is one that has been shown to exist exclusively in the monomolecular form at room

<sup>10</sup> Stieglitz, *Am. Chem. J.*, 29, 49 (1903).

<sup>11</sup> Gomberg, *Ber.*, 35, 2397 (1902).

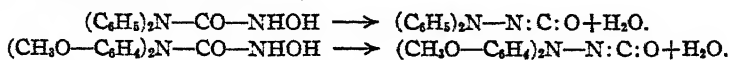
<sup>12</sup> Gomberg and Cone, *ibid.*, 37, 2403 (1904); Schlenk, Weichel, and Herzenstein, *Ann.*, 372, 10 (1910).

<sup>13</sup> McCoy and Stieglitz, *Am. Chem. J.*, 21, 116 (1899).

<sup>14</sup> Van Dam, *Rec. trav. chim.*, 18, 408 (1899); 19, 318 (1900).

temperature.<sup>15</sup> Therefore, in the univalent nitrogen derivative,  $[(C_6H_5-C_6H_4)_2C-CO-N]$ , there should be a pronounced tendency for the momentary existence of tribisphenylmethyl, and the ultimate formation of the isocyanate.

The applications of this hypothesis need not be restricted to one class of radicals that show a tendency to exist free. Since certain radicals which contain divalent nitrogen<sup>16</sup> have been prepared, a hydroxamic acid which could furnish such a group might also rearrange with considerable ease. Illustrations would be,



Benzophenone when it is treated in ether solution with potassium develops an intense color.<sup>17</sup> Since the boiling point of the ether is unchanged after complete solution of the metal, a trivalent carbon radical,  $(C_6H_5)_2C(OK)-$ , is assumed to exist in solution. In this connection, therefore, the hydroxamic acid of benzilic acid,  $(C_6H_5)_2C(OH).CO.NHOH$ , should present a somewhat complicated, but, nevertheless, a highly interesting case to develop.<sup>18</sup>

Our assumptions were corroborated to a large extent by the experimental evidence submitted in this paper. Unexpected difficulties presented themselves in the attempts to prepare the sodium and potassium salts in the diphenyl-acethydroxamic acid series. If the customary procedure, *viz.*, the addition of an alcoholic solution of sodium ethylate to an alcohol-ether solution of the benzoyl ester of the acid, *e. g.*,  $(C_6H_5)_2CH-CO-NH-OCOC_6H_5$ , was followed, no precipitation of the salt occurred, even when a very large excess of ether was used. The existence of the salt in solution was proved, but the salt could not be obtained pure. Evaporation of the alcohol and ether *in vacuo* always left a mixture of the salt with its products of decomposition and rearrangement; *viz.*, diphenylmethyl isocyanate, diphenylmethyl urethane, sodium benzoate and, also, *sym.* bi-diphenylmethyl urea, if any water was present. When this residue was extracted with cold water, and the solution filtered and boiled, there was an immediate precipitation of some *sym.* bi-diphenylmethyl urea, which is the normal reaction for salts of this character.

Similar difficulties arose in the study of triphenyl-acethydroxamic acid. The sodium or the potassium salts of the benzoyl ester could not be formed pure. The acetyl ester seemed to yield a potassium

<sup>15</sup> Schlenk, Weichel and Herzenstein, *Ann.*, 372, 11 (1910).

<sup>16</sup> Wieland, "Die Hydrazine," F. Enke, Stuttgart, 1913, p. 73.

<sup>17</sup> Schlenk and Thal, *Ber.*, 46, 2843 (1913); Schlenk and Weichel, *ibid.*, 44, 1183 (1911).

<sup>18</sup> Jones and Neuffer (THIS JOURNAL, 39, 659 (1917)), have studied the rearrangements of lact-hydroxamic acid,  $CH_3-CHOH-CO-NHOH$ , and of mandel-hydroxamic acid,  $C_6H_5CH(OH).CO.NHOH$ .

salt insoluble in ether; but subsequent tests showed that it was mixed to a large extent with triphenylmethyl isocyanate. This isocyanate, not previously described, possesses a remarkable stability, even in the presence of boiling water. Thus, when the precipitate containing the potassium salt was taken up in water, and heated, only the isocyanate separated. The cause of its sluggishness may be attributed to its insolubility in water. It reacts normally with aniline in ether to form the urea derivative.



The evidence obtained proves that there is an increase in the ease of rearrangement of the molecule as more phenyl groups are added. In solution, the potassium salt of the benzoyl or acetyl ester of monophenyl-acethydroxamic acid was comparatively stable at room temperature; a similar solution of the diphenyl compound became turbid in a short time; whereas the triphenyl derivative showed rearrangement almost immediately when it was treated with water. In the diphenyl or in the triphenyl series, it was found to be impossible to obtain a sodium or a potassium salt which failed to show the effects of extensive decomposition. For this reason, the temperature of decomposition of the pure dry salts could not be determined accurately.

The silver salts, made by the action of aqueous silver nitrate upon the cold ether solutions of the sodium or potassium salts were somewhat soluble,<sup>19</sup> but precipitated for the most part. Chromo-isomerism was displayed here. The silver salt of the benzoyl ester of diphenyl-acethydroxamic acid, when first formed, was bright yellow. In a short time, the yellow substance changed to a pure white salt. The similar salt in the triphenyl series precipitated as a white solid, but changed soon to a brilliant yellow salt.<sup>20</sup>

<sup>19</sup> The exact cause of the solubility of the sodium and of the potassium salts in alcohol with a large excess of ether is purely a matter of conjecture. There may be tautomeric forms, one soluble and the other insoluble, such as  $(C_6H_5)_2CHC=O-NK-OCOCH_3$  and  $(C_6H_5)_2CH-C(OK):N-OCOCH_3$ . It may be caused by the addition of a molecule of alcohol; thus,  $(C_6H_5)_2CH-C(OK)(OC_2H_5)-NH-OCOCH_3$ . These are suggestions, which may be correct. Salts of the alkali metals which are soluble in ether are very uncommon but not unknown. Sodium iodide behaves in this manner. Loeb, *THIS JOURNAL*, 27, 1020 (1905).

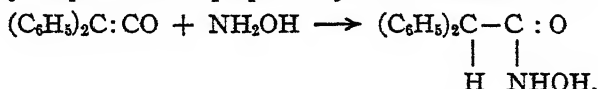
<sup>20</sup> There are many chromo-isomers on record; such, for example, as silver violurate (Hantzsch, *Ber.*, 42, 969 (1909); Henrich, "Theorien der Org. Chem.," 1918, p. 364) which is colorless when precipitated, and gradually changes through green to a dark brown. Titherley (*J. Chem. Soc.*, 71, 468 (1897); 79, 408 (1901)), reported silver benzamide to exist in an orange and in a white modification. Jones and Oesper (*THIS JOURNAL*, 36, 2208 (1914)), found chromo-isomeric silver salts among acyl derivatives of hydroxy-urethanes; e. g.,  $C_6H_5CO-O-NaAg-CO-OR$ . These salts, yellow when prepared were easily transformed into white modifications, especially if R represents *iso*-butyl, *iso*-amyl, or benzyl.

Although the salts of the alkali metals could not be isolated pure, solutions of them in water could be obtained without extensive decomposition, if the silver salts were suspended in an ice-cold solution of potassium bromide. In a few hours the reaction was complete. This constitutes a helpful modification of a reaction never before applied to hydroxamic acids.

An interesting relationship between chemical constitution and melting points is to be gained from a study of the following table. The low melting benzoyl ester of triphenyl-acethydroxamic acid is of particular interest (See experimental part, p. 2439.)

	M. Pt. °C.	Benzoyl ester. °C.	Difference. °C.
CH <sub>3</sub> CO—NHOH	87	69 or 98	18 or +11
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CO—NHOH	145	120	25
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH—CO—NHOH	173	140	33
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C—CO—NHOH	178	44–47	131–134

Two new methods of preparation of hydroxamic acids were investigated. First, the action of free hydroxylamine upon a ketene. With diphenyl ketene, the compound formed was diphenyl-acethydroxamic acid, the same in every respect as that prepared by other means. The equation is



The reaction is perfectly analogous to the addition of ammonia, or amines, to ketenes,  $R_2C:CO + H-NHR' \longrightarrow R_2CH-CO-NHR'$ . Staudinger<sup>21</sup> predicted the formation of hydroxamic acids, but stated "Die Einwirkung von Hydroxylamine, die zur Bildung von Hydroxamsäuren führen sollte, ist noch nicht untersucht."

There is another possible direction in which hydroxylamine might add to diphenyl ketene. The amide of benzoic acid would be formed;  $(C_6H_5)_2C:CO + NH_2OH \longrightarrow (C_6H_5)_2C(OH)-CONH_2$ . There are no cases recorded in which the hydroxyl group adds to ketenes in such a manner. Invariably, it combines with the carbonyl group. Hydrogen peroxide, similar in many respects to hydroxylamine, would be forced to add hydroxyl and form benzoic acid, if there were addition at all. However, Nicolet and Pelc<sup>22</sup> recently reported that the amount of benzoic acid formed when the two were mixed in anhydrous solvents was no greater "than when the ketene itself, without the addition of peroxide was treated in the same way." In the light of these results, it is not at all surprising that no trace of the amide of benzoic acid was found.

A profitable field of research is made possible by this reaction. For example, such ketenes as diphenylene ketene,  $(C_{12}H_8):C:CO$ ; methyl

<sup>21</sup> Staudinger, "Die Ketene," F. Enke, Stuttgart, 1912, p. 36.

<sup>22</sup> Nicolet and Pelc, *THIS JOURNAL*, 43, 935 (1921).

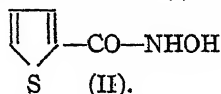
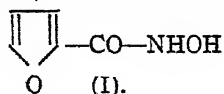
vinyl ketene,  $\text{CH}_2 : \text{CH}-\text{C}(\text{CH}_3) : \text{CO}$ ; ethyl ketene carboxylic ester,  $\text{OC} : \text{C}(\text{C}_2\text{H}_5)-\text{COOC}_2\text{H}_5$ ; carbon suboxide,  $\text{C}_3\text{O}_2$ ; and ketene, itself, with hydroxylamine, or substituted hydroxylamines, should lead to interesting results.

The second new method of preparing hydroxamic acids is a modification of the long established method in which acid chlorides are employed. Heretofore, the chloride has been allowed to act upon an aqueous solution of hydroxylamine. This always leads to side reactions, which lower the yield and augment the difficulty of purification of the desired product. When the acid chloride was dissolved in a neutral solvent, such as benzene, and a trifle more than 2 mols of free hydroxylamine was added, it was found that a quantitative yield of monohydroxamic acid resulted.



This reaction was modified later so that the preparation of free hydroxylamine was avoided. Two equivalents of pyridine or of sodium carbonate crystals was used with one equivalent of hydroxylammonium chloride in a benzene or an ether solution of the acid chloride. A quantitative yield was obtained here also.

Two heterocyclic hydroxamic acids were studied, one a derivative of furane, and the other of thiophene. The former (I) will be called



pyromucyl-hydroxamic acid; and the latter (II),  $\alpha$ -thenhydroxamic acid.<sup>23</sup> Previous work with heterocyclic hydroxamic acids is very slight. Pyromucyl-hydroxamic acid was prepared by Pickard and Neville,<sup>24</sup> and by Rimini,<sup>25</sup> but was not extensively studied. A few isolated examples in the pyrone series are known.<sup>26</sup> *Anti*-ethyl-thenhydroximic acid,  $\text{C}_4\text{H}_5\text{S}-\text{C}(\text{OC}_2\text{H}_5) : \text{NOH}$ , has been studied by Douglas.<sup>27</sup> It was not found possible to isolate this in the *syn* form. One object of our investigation was to

<sup>23</sup> Other names such as  $\alpha$ -thienyl formhydroxamic acid, or  $\alpha$ -thenoyl- $\beta$ -hydroxylamine suggest themselves. Both of these names have their shortcomings. Essentially, the compound is a derivative of thiophene, not of formhydroxamic acid; to call it a "hydroxylamine," conceals the acid nature of the substance. The difficulty could be avoided easily, if thiophene- $\alpha$ -carboxylic acid possessed a simple name. It would be entirely in keeping with both its chemical and physical properties to assign it a name similar to benzoic acid. Inasmuch as the grouping "thenoyl,"  $\text{C}_4\text{H}_5\text{S}-\text{CO}-$  is in common usage already, the name *thenoic* acid is suggested. The prefix "then" corresponds to "benz," and just as  $\text{C}_6\text{H}_5-\text{CONHOH}$  is benzhydroxamic acid, so  $\text{C}_4\text{H}_5\text{S}-\text{CONHOH}$  is  $\alpha$ -thenhydroxamic acid.

<sup>24</sup> Pickard and Neville, *J. Chem. Soc.*, 79, 847 (1901).

<sup>25</sup> Rimini, *Gazz. chim. ital.*, [2] 31, 90 (1901).

<sup>26</sup> Oliveri-Mandala, *J. Chem. Soc.*, 100, 916 (1905); 88, 428 (1911); *Atti. accad. Lincei*, [5] 14, ii, 162 (1905).

<sup>27</sup> Douglas, *Ber.*, 25, 1312 (1892).

study the chemical behavior of pyromucyl-, and of thenhydroxamic acids, since they are typical members of a legion of unstudied heterocyclic compounds.

Pickard and Neville<sup>24</sup> stated "an aqueous solution of the sodium salt" of the benzoyl ester of pyromucyl-hydroxamic acid,  $C_4H_3O-CO-NNa-O-COC_6H_5$ , "when boiled with water evolves carbon dioxide and an oil (containing nitrogen) is obtained when the solution is evaporated. The oil is presumably difurfuran-carbamide, but decomposes completely when hydrolyzed. No better success was obtained on attempting to prepare the carbamates by boiling the sodium salt with alcohols."

A year later, Curtius and Leimbach<sup>28</sup> tried to isolate *sym.* difuryl urea,  $CO(NH-C_4H_3O)_2$ , from the azide,  $C_4H_3O-CO-N_3$ , and met with only partial success. Crystals melting at  $229^\circ$ , and at  $220^\circ$  were obtained. The former was found to contain 12.01% of nitrogen, the latter 12.13%. The calculated percentage for difuryl urea is 14.56%.

In the present study, it was found that when the potassium salt,  $C_4H_3O-CO-NK-OCOC_6H_5$ , was warmed gently in water solution, and cooled at the first evidence of precipitation, the precipitate formed was the free benzoyl ester,  $C_4H_3O-CO-NH-OCOC_6H_5$ . This compound is produced by hydrolysis, not by rearrangement. When this same filtrate was heated to boiling, much carbon dioxide was evolved, and a red resinous mass precipitated; after purification, it melted at about  $210^\circ$ . This material is similar to the product found by Curtius and Leimbach.

Thenhydroxamic acid derivatives were observed to undergo a slight hydrolysis also, but rearrangement to form *sym.* di-thienyl urea was a simple matter. Curtius and Thyssen<sup>29</sup> obtained this same urea from the azide,  $C_4H_3S-CO-N_3$ . The properties of their compound check with those of ours in all respects. The normal reaction, then, is as follows,



This behavior is entirely analogous to that of the salts of dibenzhydroxamic acid.

It will be noticed that the benzoyl ester of thenhydroxamic acid is isomeric with the thenoyl ester of benzhydroxamic acid. The latter compound was prepared, so that comparative properties of the two might be observed. Melting points of the pure substance, and the temperatures at which the potassium and the silver salts decomposed were for the former  $144^\circ$ ,  $125^\circ$  and  $168^\circ$ ; for the latter,  $133^\circ$ ,  $135^\circ$  and  $165^\circ$ , respectively. The ease of rearrangement of the potassium or the sodium salts in aqueous solution was nearly identical. Too much stress should not be laid upon the temperature of decomposition of the solid salts. The figures are of importance, but the method of applying heat to determine the temperature

<sup>28</sup> Curtius and Leimbach, *J. prakt. Chem.*, [2] 65, 37 (1902).

<sup>29</sup> Curtius and Thyssen, *ibid.*, [2] 65, 17 (1902).

of decomposition influences them very much. For example, when the potassium salt of the latter compound is heated slowly there is no visible action until about  $160^{\circ}$ . However, if the tube containing the salt is suddenly thrust in a bath at  $135^{\circ}$ , there is violent decomposition. With most of the salts, however, there is a fairly definite temperature at which they explode when heat is applied gradually.

The physical and some of the chemical properties of thiophene compounds are very similar to those of corresponding benzene compounds. Thenhydroxamic acid is no exception. It melts at  $124^{\circ}$ , while benzhydroxamic acid also melts at  $124^{\circ}$ . It is of interest to note that di-thenhydroxamic acid melts much lower than di-benzhydroxamic acid. The former was found to exist in two modifications, one melting at  $105\text{--}107^{\circ}$ , and the other at  $83\text{--}86^{\circ}$ . Dibenzhydroxamic acid is reported by Lossen<sup>30</sup> to melt at  $145^{\circ}$ . Both of these heterocyclic hydroxamic acids resemble benzhydroxamic acid in that they form an acid ammonium salt,<sup>31</sup>  $(R\text{--CO--NH--O})_2\text{--H.NH}_4$ , which is difficultly soluble in water.

### Experimental Part.

#### 1. Preparation of Diphenyl-acethydroxamic acid, $(C_6H_5)_2CH.CO.NHOH$ .

**First Method.** From Ethyl Diphenyl-acetate.—Thirty g. of ethyl diphenyl-acetate was dissolved in 180 cc. of methanol which contained a little more than the calculated amount of free hydroxylamine. The hydroxylamine was liberated from 15 g. of its hydrochloride by a solution of sodium methylate, which contained 4.8 g. of sodium. To this mixture a solution of 3.3 g. of sodium in 60 cc. of methanol was added. After 10 hours, the mixture was diluted with one liter of water, and the hydroxamic acid was precipitated with dil. sulfuric acid. The filtrate, separated from this precipitate, contained a little diphenyl-acethydroxamic acid. By the addition of a solution of copper acetate to this filtrate, 4 g. of the green copper salt was obtained.

A solution of sodium carbonate was used to purify the crude diphenyl-acethydroxamic acid, since it was found to dissolve all of the diphenyl-acetic acid present, but none of the hydroxamic acid. The insoluble part was removed and washed several times with water, and when dry, weighed 35 g. The crude material melted between  $145^{\circ}$  and  $158^{\circ}$ . Recrystallization from ethyl acetate formed needle-shaped crystals melting at  $172^{\circ}$ .

Diphenyl-acethydroxamic acid is soluble in acetone, in ethyl acetate, in ethyl alcohol, and in a warm solution of sodium hydroxide. It is insoluble in water, in a solution of sodium carbonate (hot), in ligroin, in benzene, in ether, or in chloroform. An alcoholic solution yields the characteristic red color with ferric chloride.

*Analyses.* Subs., 0.1470, 0.1589;  $CO_2$ , 0.3962, 0.4321;  $H_2O$ , 0.0767, 0.0852. Calc. for  $C_{14}H_{13}O_2N$ : C, 73.98; H, 5.77. Found: C, 73.53, 74.18; H, 5.84, 6.00.

Subs., 0.3042; N, 16.8 cc. ( $24^{\circ}$  and 743.3 mm. (17.5")) 30% KOH sol. used. Calc. N, 6.17. Found: 6.08.

Diphenyl-acethydroxamic acid could not be prepared in quantity by the action of ethyl diphenyl-acetate upon free hydroxylamine. Enough was formed to give a purple coloration with ferric chloride, but in order to obtain a satisfactory yield, one mol. of sodium methylate (or its equivalent) seemed essential.

<sup>30</sup> Lossen, *Ann.*, 161, 347 (1872).

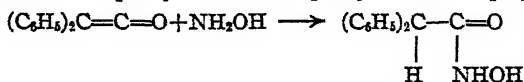
<sup>31</sup> Lossen, *ibid.*, 281, 172 (1894).



**Second Method. From Diphenyl-acetyl Chloride.**—Diphenyl-acethydroxamic acid was also prepared from diphenyl-acetyl chloride, although the method was less satisfactory because of side reactions. A solution of 1.9 g. of hydroxylammonium chloride in a small amount of water, was mixed with a solution of 2.8 g. of sodium carbonate. After carbon dioxide had escaped, 6 g. of diphenyl-acetyl chloride crystals was added and the mixture was shaken vigorously. When the reaction had apparently ceased, the product was warmed to 60°, then filtered to collect the solid. When the filtrate was acidified, half a gram of diphenyl-acetic acid (m. p. 145°) precipitated.

The residue obtained by filtration (5 g.) gave a double melting point, 155–160°, and 215–230°. Recrystallization from ethyl acetate led to the separation of diphenyl-acethydroxamic acid (m. p. 172°), and *sym.* bi-diphenylmethyl urea (m. p. 269–270°),  $\text{CO}(\text{NH}.\text{CH}(\text{C}_6\text{H}_5)_2)_2$ , which will be described later. Yield of the hydroxamic acid, 2 to 3 g.

**Third Method. From Diphenyl Ketene.**—Diphenyl ketene was prepared by Schroe-



ter's method.<sup>32</sup> Azibenzil, formed by the oxidation of 29 g. of benzil hydrazone dissolved in 120 cc. of dry benzene, was warmed to 60° in a current of dry carbon dioxide for about 3 hours, until evolution of nitrogen had ceased.

Two g. of freshly distilled hydroxylamine was suspended in a mixture of 50 cc. of absolute ether and 20 cc. of ethyl acetate, which had been carefully purified to remove traces of alcohol, water, or acetic acid. To this mixture, 100 cc. of the benzene solution of diphenyl ketene was added, while air was excluded carefully by maintaining an atmosphere of dry hydrogen gas.<sup>33</sup> Ether was employed to increase the solubility of hydroxylamine, which is insoluble in benzene. A better yield would be obtained, no doubt, if an ether solution of diphenyl ketene were used, but in this preparation the yield was of secondary interest.

After the mixture had been shaken thoroughly, the product gradually darkened. From time to time, the stopper of the flask was lifted momentarily to release the pressure, probably caused by the decomposition of some hydroxylamine. After two hours, very little pressure accumulated; so the flask was left overnight. The solvent was then distilled at the temperature of a water-bath and the residue was poured into an Erlenmeyer flask to crystallize. The crystals secured in this way were crystallized from ethyl acetate and petroleum ether. Yield, 4 g. After one recrystallization, the melting point was 169–172°.

To establish the identity of this compound and diphenyl-acethydroxamic acid prepared above, the benzoyl esters of both were made and found to possess identical properties. Both preparations melted at 140°. (See below.)

**Fourth Method. From the Copper Salt.**—Apparently, there are two forms of mono-phenyl-acethydroxamic acid. By the decomposition of the copper salt with hydrogen sulfide, Thiele and Pickard<sup>9</sup> obtained a compound melting at 121°. Phenyl-acethydroxamic acid which melted at 145° was prepared by Jones by the interaction of free hydroxylamine and ethyl phenyl-acetate. It was thought probable that a second form of diphenyl-acethydroxamic acid might be obtained, if the copper salt should be suspended in alcohol and decomposed by hydrogen sulfide, but such was not found to be the case.

**Benzoyl Ester:**  $(\text{C}_6\text{H}_5)_2\text{CH}.\text{CO}.\text{NHO}-\text{CO}.\text{C}_6\text{H}_5$ .—Three and five-tenths g. of diphenyl-acethydroxamic acid was dissolved in a warm solution of potassium hydroxide

<sup>32</sup> Schroeter, *Ber.*, **42**, 2345 (1909); Staudinger, *Ref.* 21, p. 144.

<sup>33</sup>  $\text{CO}_2$  reacts with  $\text{NH}_2\text{OH}$ .

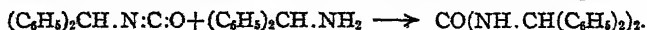
just sufficient to cause the solution of the acid. Benzoyl chloride (1.65 cc.) was added in 4 portions. The reaction mixture was constantly agitated, while a stream of cold water was played over the flask. This gave 6 g. of crude dry product. Crystallization of this material from alcohol yielded plates which melted at 139.5–141°. Three recrystallizations caused the compound to have a sharp melting point, 140–140.5°. This ester is soluble in acetone, in ethyl acetate, in chloroform and in hot alcohol; slightly soluble in ether and in benzene, and insoluble in water, in ligroin and in a cold solution of sodium hydroxide. When the solution of sodium hydroxide is warmed, rearrangement takes place. When the ester was heated a little above its melting point, the odor of isocyanate became noticeable at once.

*Analysis.* Subs., 0.5417: N, 20.6 cc. (over 40% KOH, at 26° and 740.1 mm.) Calc. for  $C_{21}H_{17}O_3N$ : N, 4.22. Found: 4.13.

*Potassium Salt.*  $(C_6H_5)_2CH.CO.NK.O.CO.C_6H_5$ .—First Method. Alcoholic potassium hydroxide was prepared of such a strength that 1 cc.  $\approx$  0.113 g. of KOH. One cc. of this reagent was added to a solution of 0.67 g. of the benzoyl ester in a mixture of 15 cc. of absolute alcohol and 10 cc. of dry ether, previously cooled to –15°. There was no precipitation when a sample of the solution was diluted largely with ether, or with petroleum ether. Part of the solution was treated with silver nitrate to form the silver salt (see p. 2435). The rest was evaporated *in vacuo* over conc. sulfuric acid. For convenience, the residue left after evaporation of the solution will be called "R."

This residue (R) was shown to consist of a mixture of the desired potassium salt, together with diphenyl-methyl isocyanate, diphenyl-methyl urethane, and potassium benzoate. The part of (R) which was soluble in ether was extracted and half of this ether solution was evaporated. A residue remained which melted at 90° to 100°. Two recrystallizations of this material from benzene and ligroin resulted in the isolation of the urethane,  $(C_6H_5)_2CH.NH.CO.OC_6H_5$ , melting at 124°. The properties of this compound were confirmed by its preparation from diphenyl-acetamide, (see below).

The other half of the portion soluble in ether was shown to contain the isocyanate,  $(C_6H_5)_2CH.NCO$ , since an ether solution of benzhydriyl-amine added to it, caused an immediate precipitate of the urea, m. p. 268–270°, according to the equation,



Benzhydriyl-amine is without action upon an ether solution of the urethane.

The residue left from (R) after ether extraction was also divided into two parts. One part was analyzed and was found to contain a much greater percentage of potassium than that calculated for the potassium salt,  $(C_6H_5)_2CH.CO.NK.O.CO.C_6H_5$ .

*Analysis.* Subs., 0.1385:  $K_2SO_4$ , 0.0441. Calc. for  $C_{21}H_{16}O_3NK$ : K, 10.58. Found: 14.30.

This would indicate the presence of potassium benzoate as an impurity.

The other part dissolved in water to give a clear solution. A portion of the solution was boiled; this caused an immediate precipitation of *sym.* bi-diphenylmethyl urea, which confirms the presence of some potassium salt of the benzoyl ester. The remainder of the solution, acidified with dil. hydrochloric acid, gave a precipitate which, by fractional crystallization from alcohol, was resolved into the original benzoyl ester of diphenyl-acethydroxamic acid, m. p. 140°, and benzoic acid, m. p. 121°.

*Second Method.* A solution of potassium ethylate prepared from metallic potassium instead of potassium hydroxide gave no different results.

An interesting observation was made concerning the extreme solubility of the potassium salt. When 0.33 g. of the benzoyl ester was suspended in a cold mixture of 3 cc. of alcohol, and 6 cc. of ether, the undissolved ester went into solution when alcoholic potash was added.

**Third Method.** About 0.36 g. of silver salt,  $(C_6H_5)_2CH.CO.NAg.O.CO.C_6H_5$  (see preparation, below) suspended in 4 cc. of ice-water, was treated with 0.12 g. of potassium bromide, dissolved in a little water. The mixture was stirred frequently. After an hour, the precipitate had assumed the yellow color of silver bromide. Ample proof of metathesis was furnished when a little of the solution was filtered, and heated. A heavy crystalline precipitate of *sym.* bi-diphenylmethyl urea (m. p. 268–270°) separated. There appears to be no record of the use of silver salts in the preparation of alkali salts of hydroxamic acid.

The reaction mixture was kept at 0° overnight. Little, if any, decomposition occurred. One-third of the solution, after filtration, was acidified. The benzoyl ester precipitated in quantity. When a second portion of this solution was allowed to stand at room temperature, a gradual precipitation of the urea took place.

A portion of the solution containing the potassium salt was treated with silver nitrate, copper acetate, and cobalt nitrate solutions. The colors of the three precipitates were white, light green, and light pink respectively. These salts were not studied further.

**Sodium Salt.**  $(C_6H_5)_2CH.CO.N.Na.O.CO.C_6H_5$ .—A convenient solution of sodium ethylate to employ is one in which 1 cc.  $\approx$  0.023 g. of sodium. To a solution of 0.3 g. of benzoyl ester in 4 cc. of absolute alcohol and 15 cc. of ether, 0.9 cc. of the sodium ethylate solution was added. (The ester was in slight excess.) Just as with the potassium salt, here, also, no precipitate could be obtained. One portion of this solution was saved for the preparation of the silver salt, (see below) while a second portion of the solution was evaporated rapidly, and the residue extracted with water. Filtration from the insoluble matter left a clear solution that soon became turbid. A precipitate of the urea derivative was formed by boiling the solution.

The remainder of the ether-alcohol solution was evaporated *in vacuo* over conc. sulfuric acid. Ether caused the extraction of a large amount of the urethane, m. p., 123–124°. The portion insoluble in ether was shown by analysis to be chiefly sodium benzoate.

**Analysis.** Subs., 0.0558:  $Na_2SO_4$ , 0.0251. Calc. for  $C_{21}H_{15}O_2NNa$ : Na, 6.51. Calc. for  $C_6H_5.COONa$ : Na, 15.97. Found: 14.56.

**Silver Salt.**  $(C_6H_5)_2CH.CO.NAg.O.CO.C_6H_5$ .—First Method: from the potassium salt. The ether-alcohol solution of the potassium salt (see p. 2434) was treated with an aqueous solution of silver nitrate. The ether layer instantly assumed a deep yellow color, but remained clear. When this solution was shaken, a *pure white* precipitate of the silver salt formed, and the yellow color of the ether layer disappeared simultaneously.

**Analysis.** Subs., 0.1164: Ag, 0.0285. Calc. for  $C_{21}H_{15}O_2NAg$ : Ag, 24.62. Found: 24.49.

A little of the white salt, suspended in ether, did not cause the ether to assume a yellow color, even when alcohol was added. Here, again, as with the sodium or the potassium salt, there is evidence of the existence of two modifications, one of which is soluble in ether and alcohol, and the other insoluble. Gradual rearrangement occurred when the salt was heated gently; the odor of isocyanate was very marked. In a small tube the salt decomposed with a puff at about 145°.

**Second Method:** from the sodium salt. A similar procedure was followed with an ether-alcohol solution of the sodium salt (see above). In this case, the ether layer became yellow in color, and the precipitate which formed was yellow as well. The color of the salt gradually changed to pure white, and, in so doing, formed needle-shaped crystals. This change of color was hastened by scratching the precipitate with a glass rod. That the color change commenced at the surface was proved; for

yellow clumps that had apparently turned white, were found still to be yellow at the center. This material, when heated on a spatula, decomposed with a puff to form the isocyanate and a residue of metallic silver was left after ignition.

**Di-acetyl Ester,  $(C_6H_5)_2CH.CO.N(CO.CH_3).O.CO.CH_3$ .**—Apparently, the normal reaction of acetic anhydride and diphenyl-acethydroxamic acid leads to the formation of the di-acetyl ester, a trihydroxamic acid, instead of the mono-acetyl ester, even when half a mol. of acetic anhydride is used. In this case, a mixture of mono- and di-acetyl derivatives is obtained. By recrystallization from alcohol, the mixture was separated only with the greatest difficulty.

To prepare the di-acetyl ester, diphenyl-acethydroxamic acid (3 g.) was dissolved in a large excess of acetic anhydride (10 cc.). This solution was kept warm for 2 hours, and the excess of acetic anhydride was then evaporated in a vacuum desiccator containing powdered alkali. The solid ester, after recrystallization from alcohol, melted at 95.5–97.5°. It is soluble in hot alcohol, in ethyl acetate, in chloroform, in acetone and in benzene. It is but slightly soluble in ether, and is insoluble in water, in ligroin, or in a solution of sodium hydroxide.

**Analysis.** Subs., 0.5008: N, 19.8 cc. (over 40% KOH at 25° and 743.8 mm. (26°)). Calc. for  $C_{18}H_{17}O_4N$ : N, 4.50. Found: 4.34.

Two g. of the di-acetyl ester was distilled in a small flask heated by a metal bath. A liquid that weighed 0.45 g. was collected when the temperature of the bath rose to between 200° and 300°. This liquid all redistilled between 120° and 138°; this fraction consisted chiefly of acetic anhydride. When the residue in the flask was heated with a free flame, a liquid distilled at about 300° and left resinous materials in the flask. When the distillate was treated with an ether solution of benzhydriyl-amine to detect any diphenylmethyl isocyanate and then diluted with an equal quantity of petroleum ether, a tardy precipitate resulted; m. p. 136–137°. This was identified as benzhydriyl-amine acetate; no *sym.* bi-diphenylmethyl urea could be found.

**Benzhydriyl-amine Acetate,  $(C_6H_5)_2CH.NH_2O.COCH_3$ .**—A sample of benzhydriyl-amine acetate was prepared by mixing an ether solution of benzhydriyl-amine with glacial acetic acid. White crystalline plates separated, which melted at 138°. The salt dissolved readily in water.

**Mono-acetyl Ester,  $(C_6H_5)_2CH.CO.NH—O—CO.CH_3$ .**—In order to avoid the formation of the di-acetyl ester, precautions had to be taken to destroy the acetic anhydride as soon as the reaction mixture showed no mono-hydroxamic acid. Ferric chloride was used as an indicator. Three g. of diphenyl-acethydroxamic acid was dissolved rapidly in an excess of warm acetic anhydride (10 cc.), and, after about 30 seconds, the reaction was stopped by the addition of 50 cc. of cold water. A white precipitate, chiefly the mono-acetyl ester, resulted. Two recrystallizations gave crystalline plates of pure substance melting at 113–113.5°.

The acetyl ester dissolves in acetone, in chloroform, in ethyl acetate, in benzene and in alcohol. It is insoluble in a cold solution of sodium hydroxide and in ligroin, and only slightly soluble in ether. When the solution of sodium hydroxide is warmed, rearrangement takes place.

**Analysis.** Subs., 0.3046: N, 14.1 cc. (over 40% KOH at 23.5° and 738.8 mm. (19°)). Calc. for  $C_{18}H_{15}O_3N$ : N, 5.20. Found: 5.09.

**Potassium Salt.**— $(C_6H_5)_2CH.CO.NK.O.CO.CH_3$ .—One-third of a gram of acetyl ester dissolved quite readily in 5 cc. of cold alcohol. The solution was diluted with 10 cc. of ether and was then chilled to –10° by means of a freezing mixture of ice and conc. sulfuric acid. To this solution, 0.6 cc. of alcoholic potash solution (see p. 2434) was added. Here again, no precipitate formed, even when an excess of ether was

added. Part of the liquid was evaporated; the residue was extracted with ether, dried and analyzed.

*Analysis.* Subs., 0.0929:  $K_2SO_4$ , 0.0293. Calc. for  $C_{16}H_{14}O_2NK$ : K, 12.72. Found: 14.15.

This high result is explained by the presence of potassium acetate, a decomposition product.

The remainder of the solution, which still contained the potassium salt, was diluted with 10 cc. of petroleum ether. There was no precipitate. If it was shaken with a dil. solution of silver nitrate in water, a white silver salt was obtained (see below).

*Sodium Salt.*—About 0.3 g. of the acetyl ester was dissolved in 2 to 3 cc. of absolute alcohol, and diluted to 15 cc. with ether. This solution, cooled with ice, was treated with 0.8 cc. of sodium ethylate solution (see p. 2435). There was a tardy precipitation that gradually became quite heavy. The addition of ether hastened its formation. This material, collected and washed with ether, was dried and analyzed. Its sodium content was found to be midway between that required for  $(C_6H_5)_2CH.CO.NNa.O.COCH_3$  and that for sodium acetate.

*Analysis.* Subs., 0.0634:  $Na_2SO_4$ , 0.0346. Calc. for  $C_{16}H_{14}O_2NNa$ : Na, 7.90. Calc. for  $CH_3.COONa$ : Na, 28.05. Found: 17.67.

*Silver Salt.*—The ether-alcohol solution of the potassium salt, when mixed with aqueous silver nitrate, formed a pure white precipitate. It was found best not to wash the salt with alcohol, since that frequently caused it to turn dark. The white precipitate was washed carefully with water, dried, and analyzed. When it was heated in a small tube, it decomposed between  $103^\circ$  and  $110^\circ$ . The isocyanate, recognized by its characteristic odor, distilled.

*Analysis.* Subs., 0.0738: Ag, 0.0213. Calc. for  $C_{16}H_{14}O_2NAg$ : Ag, 28.69. Found: 28.86.

In order to establish the identity of the products of rearrangement isolated in these reactions, they were prepared in a different manner. Some of them represent new compounds, not previously described.

*Diphenylmethyl Urethane*,  $(C_6H_5)_2CH.NH.COOC_2H_5$ .—A method, similar to that developed by Stieglitz and his students,<sup>34</sup> was employed successfully in the preparation of this urethane. A solution of sodium ethylate was made by the action of 3.42 g. of sodium upon 160 cc. of alcohol. Nine g. of diphenyl-acetamide was suspended in it, and caused to dissolve by the rapid addition of 4.1 cc. of bromine. Without filtration to remove sodium bromide, the neutral mixture was boiled for 10 minutes, after which the alcohol was distilled. The urethane was precipitated by the addition of an excess of water. Yield, 8 g. Nothing except sodium bromide was found in the filtrate. The precipitate was extracted with 50 cc. of hot benzene. One g. of material, later proved to be *sym.* bi-diphenylmethyl urea, was insoluble. When the benzene became cool, 1.8 g. of unchanged amide (m. p.  $161^\circ$ ) precipitated. The benzene filtrate contained nearly pure diphenylmethyl urethane. After evaporation of the solvent, the residue was pressed on a clay plate. Yield, 4.2 g. It may be recrystallized from a mixture of benzene and ligroin, or of alcohol and water; m. p.  $122-123^\circ$ . It is soluble in alcohol, in chloroform, in acetone, in ethyl acetate, and in benzene, but insoluble in water and in ligroin.

*Analysis.* Subs., 0.4130: N, 20.69 cc. (over 40% KOH at  $20^\circ$  and 763.9 mm. ( $16^\circ$ )). Calc. for  $C_{16}H_{14}O_2N$ : N, 5.49. Found: 5.64.

*Diphenylmethyl urea chloride*,  $(C_6H_5)_2CH.NH.CO.Cl$ .—Two g. of the urethane

<sup>34</sup> Jeffreys, *Ber.*, 30, 898 (1897); *Am. Chem. J.*, 22, 27 (1899); Polin, *Am. Chem. J.*, 19, 324 (1897).

and 1.63 g. of phosphorus pentachloride were dissolved in 10 to 15 cc. of dry chloroform. This mixture was warmed, and a current of dry hydrogen chloride was bubbled through the solution. This served to expel phosphorus oxychloride and also to prevent the decomposition of the urea chloride which would yield the more volatile isocyanate. Chloroform was added twice as the solution evaporated. Finally, when the solvent was nearly exhausted, petroleum ether was added, and the entire solution was poured through a filter. A solid mixed with oil resulted when the filtrate was evaporated.

**Diphenylmethyl Isocyanate,  $(C_6H_5)_2CH.NCO$ .**—The crude urea chloride was extracted with benzene, and the solution filtered. Some calcium oxide was placed in the flask, and the mixture was left in the stoppered flask for 3 hours. This solution contained the isocyanate (see below). After filtration, it was not purified further, but was treated at once with benzhydryl-amine to form the urea.

**Benzhydryl-amine,  $(C_6H_5)_2CH.NH_2$ .**—This compound was prepared by reducing benzophenone oxime with metallic sodium and alcohol. It has been prepared from benzophenone oxime by Goldschmidt,<sup>35</sup> who employed sodium amalgam, and also by Michaelis<sup>36</sup> from benzophenone-phenylhydrazone with metallic sodium and alcohol.

Five g. of dry benzophenone oxime was suspended in 50 cc. of absolute alcohol. The mixture was poured through a reflux condenser upon a piece of sodium which weighed 12 g. The oxime dissolved at once, and enough heat was generated to melt the sodium. A little alcohol was introduced from time to time. After 40 minutes, when all the sodium had dissolved, most of the alcohol was recovered by distillation, and water was added to the residue. After partial neutralization of the alkaline solution, benzhydryl-amine was extracted by means of ether, and the ether solution was dried over potassium hydroxide. To precipitate benzhydryl-amine hydrochloride, it was only necessary to add conc. hydrochloric acid to the ether solution. Between 5.5 and 6 g. of the salt was collected.

**Sym. bi-diphenylmethyl Urea,  $CO(NH.CH(C_6H_5)_2)_2$ .**—The benzene solution of the isocyanate (see above) was treated with an ether solution of benzhydryl-amine. There was a tardy precipitation of solid which was collected after a few hours and shown to consist of a mixture of benzhydryl-amine hydrochloride, and the urea. The former, produced because of some unchanged urea chloride, was soluble in very dilute hydrochloric acid; it melted at 276–280°. The portion insoluble in the acid melted at 266°. It was rather soluble in hot acetone and in hot ethyl acetate. Recrystallization from either of these solvents produced fine needle-shaped crystals of the urea which melted at 269.5–270°.

**Analysis.** Subs., 0.3246: N, 19.90 cc. (20° and 763.9 mm. (16°)). Calc. for  $C_{24}H_{24}ON_2$ : N, 7.14. Found: 7.07.

## 2. Triphenyl-acethydroxamic Acid.



**Triphenyl-acetyl chloride,  $(C_6H_5)_3C.COCl$ .**—Schmidlin and Hodgson<sup>37</sup> prepared triphenyl-acetyl chloride from triphenyl-acetic acid, acetyl chloride and phosphorus pentachloride. In the same year Bistrzycki and Landtwig<sup>38</sup> described a method of preparation in which phosphorus oxychloride was used as a solvent, instead of acetyl chloride.

It may be prepared much more simply with thionyl chloride as the chlorinating agent. Three g. of triphenylacetic acid and 10 cc. of thionyl chloride were placed

<sup>35</sup> Goldschmidt, *Ber.*, 19, 3233 (1886).

<sup>36</sup> Michaelis, *ibid.*, 26, 2168 (1893).

<sup>37</sup> Schmidlin and Hodgson, *ibid.*, 41, 438 (1908).

<sup>38</sup> Bistrzycki and Landtwig, *ibid.*, 41, 687 (1908).

in a small flask equipped with an air condenser, and gently warmed until solution was complete. The liquid was boiled for about 5 minutes after gas evolution (sulfur dioxide and hydrogen chloride) had ceased. Then, it was cooled and poured upon crushed ice to decompose any excess of thionyl chloride. (If larger quantities were employed, it would be better of course, to recover the thionyl chloride by distillation.) The solid triphenylacetyl chloride was filtered, washed with a little cold water, pressed upon a porous plate, and then dried in a vacuum desiccator. Without further treatment, the material obtained was pure enough for most purposes. It melted at  $127^{\circ}$ . The yield was practically quantitative.

Thionyl chloride readily dissolved both triphenylacetyl chloride, and ethyl triphenylacetate, and it was without action upon either one.

**Triphenylacethydroxamic Acid.**—Two and five-tenths g. of triphenylacetyl chloride was dissolved in 40 cc. of dry benzene. This was poured into a flask containing 2.5 g. of free hydroxylamine. The mixture was agitated at frequent intervals during an hour, and then was put aside until the next day. Since there was no precipitation of hydroxamic acid, the benzene layer was decanted from the excess of hydroxylamine, placed in a distilling flask, and the solvent was distilled. An oil remained which crystallized readily when it became cool. Petroleum ether caused an additional precipitate. More than 2 g. of crystals was obtained. The crude substance melted at  $172^{\circ}$ .

Triphenylacethydroxamic acid is soluble in a warm solution of sodium hydroxide, in benzene, in acetone, in ethyl acetate and in alcohol. It is insoluble in ligroin, and in water. Recrystallization from ether produced a pure product which melted at  $175\text{--}176^{\circ}$ .

An alcoholic solution, treated with ferric chloride, gave the usual red color reaction. Furthermore, copper acetate formed a light green copper salt.

*Analysis.* Subs., 0.3858: N, 16.14 cc. (over 40% KOH at  $21.8^{\circ}$  and 758.9 mm. ( $18^{\circ}$ )). Calc. for  $C_{26}H_{17}O_2N$ : N, 4.62. Found: 4.75.

Attempts to prepare triphenylacethydroxamic acid by the action of free hydroxylamine upon ethyl triphenylacetate,  $(C_6H_5)_3C.CO.OC_2H_5$ , resulted in failure. There was no action, even when an excess of sodium ethylate was present. In all cases the ester was recovered unchanged.

When triphenylacetyl chloride was employed with a mixture of hydroxylamine and sodium carbonate in water, it was very difficult to purify the triphenylacethydroxamic acid.

**Benzoyl Ester,**  $(C_6H_5)_3C.CO.NH.O.CO.C_6H_5$ .—First Method. One-tenth g. of triphenylacethydroxamic acid was fused with a considerable excess of benzoic anhydride until a sample gave no reaction with ferric chloride. The excess of anhydride was then extracted several times with warm ligroin ( $50^{\circ}$ ). An oil was left which refused to solidify in the course of a week. It was extracted with a very dilute, cold solution of sodium hydroxide. This solution was filtered and acidified immediately. A white solid precipitated, m. p.  $40\text{--}50^{\circ}$ . When this process was repeated the benzoyl ester was obtained in a somewhat purer state. It melted between  $44^{\circ}$  and  $47^{\circ}$  for the most part, but there was a little that did not melt until the temperature reached  $70^{\circ}$ . It is highly probable that, even at this low temperature, the ester decomposed to a slight extent into benzoic acid and triphenylmethyl isocyanate, which may account for the anomalous melting point (see p. 2429).

This low-melting ester was found to be extremely soluble in organic solvents. From benzene solution, petroleum ether precipitated it as an oil which could not be made to crystallize, even after the removal of the solvent.

By careful hydrolysis with alkalis, it was possible to convert part of the ester into triphenylacethydroxamic acid. The greater tendency by far, however, was

rearrangement of the salt in solution, not to form the urea derivative, as would be anticipated, *but to give the isocyanate*,  $(C_6H_5)_3C.NCO$ .

**Second Method.** Because of the instability of the sodium salt of the benzoyl ester of triphenylacethydroxamic acid, this method (Schotten-Baumann reaction) is less successful than the first method. One and six-tenths g. of triphenylacethydroxamic acid was dissolved in 15 cc. of water that contained 0.23 g. of sodium hydroxide. The solution was cooled in a stream of tap water, and 0.6 cc. of benzoyl chloride was added in 3 portions.

No attempt was made to purify the sticky solid. Instead, it was washed thoroughly with water, then dried, and converted into its salts.

**Potassium Salt.**  $(C_6H_5)_3C.CO.NK.O.CO.C_6H_5$ .—The crude benzoyl ester was dissolved in 1.5 cc. of absolute alcohol. This solution was treated with a solution of potassium hydroxide (0.11 g.) in alcohol. Since 20 cc. of ether caused no precipitation of salt, a solution of silver nitrate in water was added. This gave the silver salt.

**Silver Salt.**  $(C_6H_5)_3C.CO.NAg.O.CO.C_6H_5$ .—A white precipitate formed, which turned canary-yellow in a short time. It was filtered and washed thoroughly with water, and with ether. In a small tube, this salt became gray in color at  $120^\circ$ ; it was black at  $160^\circ$ ; and at  $195^\circ$  it melted with much decomposition.

**Analysis.** Subs., 0.1444: Ag, 0.0300. Calc. for  $C_{27}H_{20}O_2NAg$ : Ag, 20.98. Found: 20.85.

**Acetyl Ester,**  $(C_6H_5)_3C.CO.NH.O.CO.CH_3$ .—A large excess of warm acetic anhydride (about 3 cc.) was used to dissolve 0.6 g. of triphenylacethydroxamic acid. In about half a minute a test with ferric chloride showed that the reaction was complete. In order to stop any further action which might lead to the formation of a di-acetyl ester, 10 cc. of cold water was added to decompose any unused anhydride. In a short time, the acetyl ester solidified to form a white solid. It was filtered and dried. Very few impurities were present in this crude material. One recrystallization from a mixture of 2 cc. of benzene and 10 cc. of ligroin gave a pure product that melted at  $133.5$ – $134^\circ$ . The ester was very soluble in most common organic solvents. The yield was quantitative.

**Analysis.** Subs., 0.2156: N, 7.62 cc. ( $20^\circ$  and 762.2 mm.). Calc. for  $C_{22}H_{19}O_2N$ : N, 4.06. Found: 4.08.

**Potassium Salt.**  $(C_6H_5)_3C.CO.NK.O.CO.CH_3$ .—When 0.38 g. of the acetyl ester was dissolved in a small quantity of absolute alcohol and neutralized with 0.55 cc. of alcoholic caustic potash (0.062 g. of potassium hydroxide), a little ether caused the separation of a gelatinous precipitate, which was collected upon a filter. The material would not dissolve to give a clear solution in cold water. It was evident that the unstable potassium salt suffered rearrangement in solution, because the solution, turbid at first, rapidly became white and opaque. When the solution was boiled, the potassium salt was decomposed completely; triphenylmethyl isocyanate was precipitated. The dry salt decomposed slightly at  $112^\circ$ . At  $165^\circ$  there was a vigorous evolution of gas.

**Analyses.** Subs., 0.0400, 0.1253:  $K_2SO_4$ , 0.0080, 0.0252. Calc. for  $C_{22}H_{18}O_2NK$ : K, 10.19. Found: 8.98, 9.03.

**Sodium Salt.**—Sodium ethylate and ether did not cause a precipitate when added to a solution of the acetyl ester in alcohol. Accordingly, the solution was treated with an aqueous solution of silver nitrate to form the silver salt.

**Silver Salt.**—This was thrown down at once as a yellow precipitate, but the quantity was insufficient to warrant an analysis. When heated upon a spatula it decomposed at a fairly high temperature and left a residue of metallic silver.

**Triphenylmethyl Isocyanate,**  $(C_6H_5)_3C.NCO$ .—When a solution of the potassium



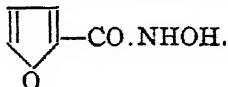
salt of the acetyl ester of triphenylacethydroxamic acid was boiled for a short time with water, an oil was formed. In the course of a few hours this oil solidified. It was collected, and washed with water. The isocyanate was very soluble in organic solvents, even in ligroin. It was dissolved in petroleum ether, filtered into an open dish, and most of the solvent evaporated in a vacuum desiccator. White crystals were formed in this manner, m. p. 85–87°.

*Analysis.* Subs., 0.1518: N, 6.72 cc. (17° and 757 mm. (18°)). Calc. for  $C_{23}H_{18}ON$ : N, 4.91. Found: 5.12.

The solubility in petroleum ether, and the low melting point are sufficient evidence that this compound could not be *sym.* bi-triphenylmethyl urea,  $CO(NH.C(C_6H_5)_3)_2$ . Although E. von Meyer and P. Fischer<sup>29</sup> claim to have prepared this urea, none of its properties, not even the melting point, was described. It can be predicted, however, that the melting point is very high.

In order to prove that the material in hand was the isocyanate, it was dissolved in ether, and treated with the calculated quantity of aniline, also dissolved in ether. Upon evaporation of the ether, a white solid was left which melted sharply at 242°. This was anticipated, since phenyl-triphenylmethyl urea,  $C_6H_5.NH-CO.NH.C(C_6H_5)_3$ , which has been prepared<sup>29</sup> previously, was known to melt at that temperature.

### 3. Pyromucyl-hydroxamic Acid.



The procedure described by Pickard and Neville<sup>24</sup> for the preparation of pyromucyl-hydroxamic acid employed ethyl pyromucate and hydroxylamine in alcoholic solution. It was purified through the medium of the insoluble copper salt. Our modification of the method consists in the addition of a mol of sodium ethylate, and the direct recovery of the hydroxamic acid without the intermediate formation of the copper salt.

Thirty g. of methyl pyromucate was poured into 150 cc. of a methanol solution of free hydroxylamine which had been liberated from 19.5 g. of its hydrochloride by a solution of sodium methylate containing 6.4 g. sodium. A solution of 5.4 g. of sodium in 70 cc. of methanol was then added to the mixture and, after 10 hours, as light excess of conc. hydrochloric acid was introduced. Sodium chloride was separated and the methanol removed by distillation *in vacuo*. An oil was left which solidified after a few hours in a vacuum desiccator. One crystallization from water brought the melting point to 119–122°. Twenty-four g. of this material was obtained. Three g. of the copper salt was precipitated from the solvent used in recrystallization.

The acid is soluble in alcohol, in ethyl acetate, and in water. In benzene, in chloroform, in carbon disulfide, in ligroin, and in ether it is insoluble.

*Ammonium Salt.*  $(C_4H_5O.CO.NH.O)_2H.NH_4$ .—Ammonium hydroxide caused the precipitation of beautiful crystalline plates, when added to an aqueous solution of pyromucyl-hydroxamic acid. (Cf. p. 2444.) This precipitate was soluble either in an excess of ammonium hydroxide, or in dilute acid, which indicated that the salt is the acid salt and not the normal salt. In the former case, the normal salt is undoubtedly obtained, whereas with acids, the soluble pyromucyl-hydroxamic acid is restored. The salt melted at 130–131°, with considerable gas evolution. The analysis gave the same values whether the salt was prepared in this manner, or in the absence of water, by the action of dry ammonia upon an alcohol-ether solution of pyromucyl-hydroxamic acid.

<sup>29</sup> von Meyer and Fischer, *J. prakt. Chem.*, [2] 82, 521 (1910).

*Analyses.* (I) Prepared in the presence of water. Subs., 0.1114: N, 15.9 cc. (over 40% KOH at 27° and 737.9 mm.); (II) prepared in the absence of water; subs., 0.2126: N, 27.58 cc. (17.3° and 772.6 mm. (15°)). Calc. for  $C_{10}H_{12}O_5N_2$ ; N, 15.49. Found: (I) 15.41, (II) 15.30.

**Benzoyl Ester,  $C_6H_5O.CO.NH.OCO.C_6H_5$ .**—Pickard and Neville<sup>40</sup> stated that this derivative "is precipitated when an aqueous solution of the hydroxamic acid is shaken with the calculated quantity of benzoyl chloride, and sodium acetate." Potassium hydroxide was found to be far superior to sodium acetate. Three g. of pyromucyl-hydroxamic acid, and 1.3 g. of potassium hydroxide were dissolved in 20 cc. of water, and 2.7 cc. of benzoyl chloride was added in 4 portions. A quantitative yield of the benzoyl ester resulted. After recrystallization from alcohol, the compound melted at 140°. <sup>41</sup>

**Preparation of Salts.**—The following general method was employed in the preparation of the potassium and the sodium salts of the esters. Alcoholic solutions of sodium ethylate, or of potassium ethylate were added to concentrated alcoholic solutions of the esters. The salt usually precipitated at once. It was found advantageous to add the alcoholate in a slight excess. Three or four volumes of ether were added to effect a complete separation of the salt.

To prepare the silver salts, it was necessary only to add a solution of silver nitrate in water, to an aqueous solution of the potassium salt. In most cases this could be done at room temperature, but in a few cases a lower temperature was required to inhibit any hydrolysis.

**Potassium Salt,  $C_6H_5O.CO.NK.O.CO.C_6H_5$ .**—The appearance of the dry salt was unchanged after 8 months. In a small tube, it puffed at 125°.

*Analysis.* Subs., 0.4337:  $K_2SO_4$ , 0.1380. Calc. for  $C_{12}H_9O_4NK$ : K, 14.52. Found: 14.28.

**Sodium Salt.**<sup>42</sup>—This salt was white when first formed, but in 3 months the color was distinctly yellow.

**Silver salt.**—The silver salt was pure white.

*Analysis.* Subs., 0.1289: Ag, 0.0413. Calc. for  $C_{12}H_9O_4NAg$ : Ag, 31.92. Found: 32.04.

All of these salts showed a decided tendency to undergo hydrolysis. The potassium salt, dissolved in cold water, gave a ferric chloride color test in a very short time. Similarly, a little of the silver salt suspended in boiling water, caused a separation of black silver, a reaction characteristic of monohydroxamic acids.

When a 0.5 *M* solution of the potassium salt was warmed carefully to about 70°, crystals were precipitated which were unmistakably identified as the benzoyl ester. By careful application of heat, the filtrate gave a still more abundant yield of the same ester. If the filtrate from this precipitate was heated to boiling, a red resinous mass accompanied by the evolution of much carbon dioxide, was formed. This was dried, and then recrystallized twice from a mixture of alcohol and ether. After this treatment, it was still colored. The material darkened at 180°, and melted at 210° with decomposition. This is presumably *sym. difuryl urea*, although enough was not obtained for analysis.

If the solution of the potassium salt was heated immediately to boiling, the same resinous mass was produced, but the separation of the benzoyl ester did not occur.

**Acetyl Ester,  $C_4H_5O.CO.NH.O.COCH_3$ .**—Three g. of pyromucyl-hydroxamic acid

<sup>40</sup> Ref. 24, p. 848.

<sup>41</sup> That obtained by Pickard and Neville melted at 134°.

<sup>42</sup> This salt was previously prepared by Pickard and Neville.

and an excess (3 cc.) of acetic anhydride were warmed until solution occurred. The excess of anhydride was evaporated in a vacuum desiccator. The white crystalline mass was pressed upon a porous plate, and recrystallized from water. It melted at 95–96°. This ester is soluble in alcohol, in ethyl acetate, in chloroform, in acetone, in hot benzene and in hot water. It is insoluble in ether and in ligroin.

*Analyses.* Subs., 0.3526, 0.2920: N, 26.1 cc. (over 40% KOH at 24.5° and 740.3 mm. (26.5°)), 21.6 cc. (26° and 743.8 mm.). Calc. for  $C_7H_7O_4N:N$ , 8.28. Found: 8.09, 8.08.

*Potassium salt.*—The appearance of this salt was unchanged after standing for 8 months.

*Analysis.* Subs., 0.3325:  $K_2SO_4$ , 0.1403. Calc. for  $C_7H_6O_4NK$ : K, 18.87. Found: 18.98.

*Sodium salt.*—Alcoholysis of the salt could not be prevented, even when it was prepared at 0°. The salt of pyromucyl-hydroxamic acid was shown to be present when it was treated with a solution of ferric chloride, by the appearance of a deep purple color. It was expected, therefore, that the percentage of sodium in the sample would be higher than that required by the sodium salt of the acetyl ester of pyromucyl-hydroxamic acid.

*Analyses.* Subs., 0.2667, 0.1064:  $Na_2SO_4$ , 0.1133, 0.0436. Calc. for  $C_7H_6O_4NNa$ : Na, 12.14. Found: 13.75, 13.27.

A still higher sodium content was found when methanol, at 0°, replaced ethyl alcohol in its preparation. After 3 months the salt was bright yellow in color.

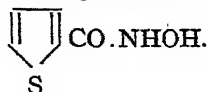
*Analysis.* Subs., 0.1032:  $Na_2SO_4$ , 0.0470. Found: Na, 14.75.

*Silver salt.*—It was necessary to prepare this derivative at 0°. When the salt was prepared at room temperature, hydrolysis to give the monohydroxamic acid was indicated by the formation of a black precipitate of metallic silver.

*Analysis.* Subs., 0.0982: Ag, 0.0382. Calc. for  $C_7H_6O_4NAg$ : Ag, 39.09. Found: 38.90.

Both the rearrangement and the hydrolysis of these salts were perfectly analogous to the behavior shown by the salts of the benzoyl ester; except that in this case the tendency to hydrolyze appeared greater.

#### 4. Thenhydroxamic Acid.



*First Method.*—A solution of free hydroxylamine in methanol was prepared by mixing Solutions A, and B, composed, respectively of, 4.90 g. of hydroxylammonium chloride in 50 cc. of methanol, and 35 cc. of methanol to which 1.67 g. of sodium had been added. Sodium chloride was removed by filtration.

Nine and six-tenths g. of thenoic ethyl ester,  $C_4H_5S-CO.OC_2H_5$ , previously purified by distillation *in vacuo*, was added to the alcoholic solution of hydroxylamine, followed by one mol of sodium methylate (1.42 g. of sodium in 30 cc. of methanol), and the mixture was allowed to stand overnight. Then 5 cc. of conc. hydrochloric acid was used to precipitate the sodium as sodium chloride. The solvent distilled *in vacuo*, after filtration to remove the salt, left a thick liquid which was placed in a vacuum desiccator to crystallize. The solid obtained in this way, crystallized from water, melted at 105–113°. Recrystallization from toluene resulted in pure material, m. p. 123–124.5°.

A water solution of thenhydroxamic acid is acid to litmus. With ferric chloride

and copper acetate, it reacts in the normal manner, to give respectively, a purple colored liquid, and a grass-green copper salt. The acid is soluble in alcohol, in hot toluene, in hot benzene, in chloroform, and in water. It is insoluble in ether and in ligroin. With isatin, and warm sulfuric acid the red color characteristic of thiophene derivatives is produced.

*Analysis.* Subs., 0.2259: N, 19.12 cc. (over 40% KOH at 18.5° and 757.8 mm.). Calc. for  $C_8H_5O_2NS$ : N, 9.78. Found: 9.74.

Isolation of thenhydroxamic acid through the medium of the copper salt and hydrogen sulfide was found to be successful, but the procedure is not to be recommended.

The Preparation of  $\alpha$ -Thenoyl Chloride,  $C_8H_5S.COCl$ .—Thenoyl chloride has always been prepared from thenoic acid by the action of phosphorus pentachloride.<sup>43</sup> A much simpler, and smoother preparation follows if thionyl chloride,  $SOCl_2$ , is employed instead of the phosphorus compound.

Six g. of  $\alpha$ -thenoic acid was warmed with 16 cc. of thionyl chloride until the gas evolution showed that the reaction was complete, when the two chlorides were separated by fractional distillation. Thenoyl chloride all distilled between 206° and 210°; yield, 6 g.

$\alpha$ -Thenhydroxamic Acid. Second method.—A solution of 0.3 g. of sodium carbonate, and 0.2 g. of hydroxylammonium chloride in 2.5 cc. of water was shaken with 0.3 g. of thenoyl chloride. Di-thenhydroxamic acid  $C_8H_5S.CO.NH.O.CO.C_8H_5S$  (see p. 2445) precipitated from the solution, whereas thenhydroxamic acid did not. To recover the latter, the filtrate was made slightly acid with acetic acid, and treated with copper acetate solution. The light green copper salt precipitated, although the green color of the solution showed that it possessed a rather high degree of solubility. The filtrate still gave an intense ferric chloride reaction.

The precipitate of di-thenhydroxamic acid was recrystallized from alcohol and water. It melted at 105–107°. We did not try to prepare thenhydroxamic acid by our new method, *viz.*, by the action of free hydroxylamine and a benzene solution of thenoyl chloride. No side reactions would be anticipated in this case.

*Ammonium Salt.*  $(C_8H_5S.CO.NH.O)_2H.NH_4$ .—This difficultly soluble acid salt was prepared in exactly the same way as the similar furan salt, (p. 2441) and showed the similar property of dissolving either in ammonia, or in hydrochloric acid. For analysis, the salt was precipitated from an alcohol-ether solution of thenhydroxamic acid by dry ammonia. It melted, with decomposition, at 142–143°.

*Analysis.* Subs., 0.1172: N, 13.95 cc. (21° and 769 mm. (20°)). Calc. for  $C_{10}H_{10}O_4N_2S_2$ : N, 13.85. Found: 13.75.

*Benzoyl Ester*,  $C_8H_5S.CO.NH.O.CO.C_6H_5$ .—Two g. of thenhydroxamic acid, and 0.8 g. of potassium hydroxide were dissolved in 10 cc. of water. This solution, agitated with 1.7 cc. of benzoyl chloride, gave a precipitate which was recrystallized from alcohol. The needle shaped crystals so obtained melted sharply at 143–144°, with decomposition. It is soluble in alcohol, in acetone and in ethyl acetate, and is insoluble in ligroin, or in cold water.

*Analysis.* Subs., 0.4336 g.: N, 21.97 cc. (at 21° and 758.6 mm. (at 19°)). Calc. for  $C_{12}H_9O_4NS$ : N, 5.67. Found: 5.77.

*Potassium Salt.*—The general method described upon p. 2422, was used also to prepare the salts in this series. The potassium salt was pure white. When it was heated in a small dry tube, it became yellow at 121° and decomposed with a faint puff at 125–127°.

*Analysis.* Subs., 0.5313:  $K_2SO_4$ , 0.1626. Calc. for  $C_{12}H_9O_4NSK$ : K, 13.71. Found: 13.73.

<sup>43</sup> V. Meyer and Kreis, *Ber.*, 16, 2174 (1883); Peter, *Ber.*, 18, 543 (1885).

*Sodium Salt.*—When slowly heated, the sodium salt decomposed mildly between 155° and 160°.

*Analysis.* Subs., 0.2388:  $\text{Na}_2\text{SO}_4$ , 0.0631. Calc. for  $\text{C}_{12}\text{H}_5\text{O}_2\text{NSNa}$ : Na, 8.54. Found: 8.55.

*Silver Salt.*—The silver salt decomposed between 163° and 168°. Above this temperature thienyl isocyanate distilled from the tube.

*Analysis.* Subs., 0.2364: Ag, 0.0723. Calc. for  $\text{C}_{12}\text{H}_5\text{O}_2\text{NSAg}$ : Ag, 30.47. Found: 30.58.

*Rearrangement of the Salts.*—A 0.5*M* solution of the potassium salt in water was boiled. The solution darkened, and di-thienyl urea precipitated as a gray-violet crystalline mass.<sup>44</sup> It was collected and recrystallized from acetic acid. The melting point was 224–225°.

The filtrate was acidified and the precipitate obtained was crystallized fractionally from dilute alcohol. Crystals melting at 140–144° separated at first. This material was the benzoyl ester, which must have been formed by hydrolysis of the salt. Benzoic acid was left in the filtrate. The ratio of the urea to the benzoyl ester was about 4:1.

*Acetyl Ester*,  $\text{C}_6\text{H}_5\text{S.CO.NH.O.CO.CH}_3$ .—Three-tenths g. of pure thenhydroxamic acid was warmed in an open glass dish with 0.2 g. of acetic anhydride. As soon as solution had taken place, the dish was placed in a vacuum desiccator to remove the excess of anhydride. The white solid obtained was recrystallized from benzene. The melting point was sharp at 96.5–97°; yield, quantitative. The ester is soluble in alcohol, in ethyl acetate, and in hot benzene, but is insoluble in cold benzene and in ligroin.

*Analysis.* Subs., 0.3242: N, 21.47 cc. (over 40% KOH at 17.8° and 760.3 mm. (15°)). Calc. for  $\text{C}_7\text{H}_7\text{O}_2\text{NS}$ : N, 7.57. Found: 7.66.

*Potassium Salt.*—No precautions were necessary to prepare the potassium salt

*Analysis.* Subs., 0.3099:  $\text{K}_2\text{SO}_4$ , 0.1215. Calc. for  $\text{C}_6\text{H}_5\text{O}_2\text{NSK}$ : K, 17.51. Found 17.49.

*Sodium Salt.*—Ice-cold solutions were essential in the preparation of the sodium salt. Otherwise, alcoholysis to yield the monohydroxamic acid occurred.

*Analysis.* Subs., 0.0609:  $\text{Na}_2\text{SO}_4$ , 0.0209. Calc. for  $\text{C}_7\text{H}_5\text{O}_2\text{NSNa}$ : Na, 11.10. Found: 11.11.

*Silver Salt.*—Because of hydrolysis, a water solution of the sodium salt could not be used to prepare the silver salt. A black precipitate of silver always resulted. With the potassium salt, however, the preparation was entirely successful.

*Analysis.* Subs., 0.1481: Ag, 0.0548. Calc. for  $\text{C}_7\text{H}_5\text{O}_2\text{NSAg}$ : Ag, 36.94. Found: 37.00.

These salts all puffed at a comparatively high temperature. A pronounced odor of thienyl isocyanate was always noticed. When water solutions of the salts were boiled, di-thienyl urea separated instantly. However, this was always accompanied by an unavoidable hydrolysis to form the acetyl ester and a second hydrolysis to give thenhydroxamic acid.

*Thenoyl Ester*, (Di-thenhydroxamic Acid),  $\text{C}_6\text{H}_5\text{S.CO.NH.O.CO.C}_6\text{H}_5\text{S}$ .—One preparation of this ester (Cf. p. 2444) which resulted in the high-melting modification (see below) has already been described.

Three g. of thenhydroxamic acid, and 1.18 g. of potassium hydroxide were dissolved in 15 cc. of water. The ice-cold mixture was treated with 3 portions (1 g. each)

<sup>44</sup> *Sym.* di-thienyl urea was found by Curtius and Thyssen<sup>39</sup> to be gray-violet in color, even after 7 recrystallizations from solvents with animal charcoal; m. p. 224°.

of thenoyl chloride. A precipitate which weighed 2.7 g. was collected; m. p. between 80° and 88°.

The filtrate was found to be acid in reaction, and to contain some unchanged thenhydroxamic acid. It was therefore made slightly alkaline with sodium hydroxide and treated with 2 cc. of thenoyl chloride. The resulting precipitate melted at 90–100° and weighed 1.4 g. When the filtrate was acidified, an appreciable quantity of thenoic acid separated.

The crude precipitates, (m. p. 80–100°) were combined and recrystallized from benzene. Crystals which melted between 83° and 86° were obtained. Later a re-determination of the melting point of this same sample indicated that a transformation to a higher-melting modification had taken place. The melting point ranged from 100° to 104°.

When alcohol was used as the solvent, the high melting modification separated first. There was an indication of softening at 95°, but the melting point at 102–104° was quite distinct.

Both of these compounds responded to all the reactions expected of di-thenhydroxamic acid.<sup>48</sup> They both formed salts; neither one gave a color test with ferric chloride, but after hydrolysis both showed an intense purple color with this reagent. The purest sample of the high-melting form melted at 105–107°. Its isomer melted at 83–86°. Both were soluble in alcohol, in ethyl acetate, and in hot benzene. In water and in ligroin they were insoluble.

*Analyses.* (I) Low-melting modification; subs., 0.3339: N, 16.90 cc. (16.5° and 762.0 mm.); (II) high-melting modification; subs., 0.4288: N, 19.60 cc. (18.5° and 769.1 mm. (16°)). Calc. for  $C_{10}H_7O_2NS_2$ : N, 5.53. Found: (I) 5.90, (II) 5.35.

*Potassium Salt.*  $C_4H_5S.CO.NK-O.CO.C_4H_5S$ .—The salts were all prepared from di-thenhydroxamic acid melting at 102–104°. In a small tube, the temperature of decomposition of the potassium salt was 122°.

*Analysis.* Subs., 0.1988:  $K_2SO_4$ , 0.0584. Calc. for  $C_{10}H_7O_2NS_2K$ : K, 13.42. Found: 13.18.

*Sodium Salt.*—There was no evident alcoholysis, when this last was prepared at room temperature. At 142° the dry salt decomposed.

*Analysis.* Subs., 0.0797:  $Na_2SO_4$ , 0.0206. Calc. for  $C_{10}H_7O_2NS_2Na$ : Na, 8.36. Found: 8.37.

*Silver Salt.*—An abundant white precipitate of the silver salt of di-thenhydroxamic acid resulted when aqueous solutions of the potassium salt and silver nitrate were mixed. It decomposed at 155°.

*Analysis.* Subs., 0.1253: Ag, 0.0376. Calc. for  $C_{10}H_7O_2NS_2Ag$ : Ag, 29.96. Found: 30.01.

When boiled with water, both the potassium and the sodium salts gave a dense precipitation of sym. di-thienyl urea. Water solutions of the pure salts did not readily undergo hydrolysis or rearrangement.

### 5. Benzhydroxamic Acid.

The new method of preparation of hydroxamic acids, (see p. 2430) namely, by the use of the acid chloride in benzene, was successfully employed in the preparation of benzhydroxamic acid from benzoyl chloride.

*First Method.*—Six and five-tenths g. of benzoyl chloride was dissolved in 70 cc. of dry benzene. Upon the addition of 3.3 g. of free hydroxylamine a dense precipitate of benzhydroxamic acid was formed. The reaction mixture was shaken vigorously,

<sup>48</sup> Lossen, *Ann.*, 281, 289 (1894).

and then set aside for a few hours until the odor of benzoyl chloride had disappeared. Less than half a gram of benzhydroxamic acid was recovered from the benzene filtrate. One recrystallization of the solid from hot toluene removed hydroxylammonium chloride and yielded a pure product, m. p. 124°. This is identical with the material described by Lossen.<sup>30</sup> No evidence of the higher melting di-benzhydroxamic acid was observed.

**Second Method.**—Benzhydroxamic acid was also prepared in excellent yields, from benzoyl chloride, dissolved in organic solvents, with hydroxylammonium chloride instead of free hydroxylamine. An intimate mixture of anhydrous sodium carbonate (2.1 g.) and hydroxylammonium chloride (1.4 g.) was suspended in 50 cc. of ether. When 2.8 g. of benzoyl chloride was added there was little action, but it became more vigorous when 3.5 cc. of water was added. In about half an hour the reaction was complete. The ether solution was filtered into a distilling flask, and most of the solvent was removed. When this residue was cooled, an abundant crystalline mass precipitated. This was filtered, washed with a little ether, and pressed upon a porous plate. The benzhydroxamic acid melted at 124–125° without further purification. Yield, nearly quantitative.

Similarly, benzhydroxamic acid was obtained in quantitative yields when pyridine was substituted for sodium carbonate. Benzene was used instead of ether in this case.

**Thenoyl Ester of Benzhydroxamic Acid,  $C_6H_5.CO.NH.O.CO.C_4H_9S$ .**—Two and a half g. of benzhydroxamic acid dissolved in 25 cc. of water was neutralized with 0.7 g. of potassium hydroxide. Three portions of 1 g. each of thenoyl chloride were added to this solution. The precipitate was filtered, and washed with water; yield, 2 g. When it was recrystallized from ethyl acetate, it gave white needles which melted at 133.0–133.5°. The ester is soluble in alcohol, in acetone, in ethyl acetate and in hot benzene. It is insoluble in cold benzene, in ligroin and in water.

**Analysis.** Subs., 0.1547: N, 7.70 cc. (over 40% KOH at 15° and 763 mm.). Calc. for  $C_{12}H_9O_2NS$ : N, 5.67. Found: 5.85.

**Potassium Salt.  $C_6H_5.CO.NK.O.CO.C_4H_9S$ .**—When 0.32 g. of the thenoyl ester was dissolved in a mixture of 2 cc. of alcohol and 1 cc. of ether, the potassium salt was precipitated by the addition of 0.7 cc. of an alcoholic solution of potassium hydroxide (0.08 g. KOH). Five cc. of ether caused further precipitation.

A water solution of this salt became turbid in a short time, when left at room temperature. When the solution was boiled, a crystalline precipitate of *sym.* diphenyl urea, m. p. 236–238°, was formed.

The dry potassium salt puffed vigorously at 135–140°, providing the tube containing it was thrust into a bath previously heated to that temperature. However, when the tube was gradually warmed, a mild decomposition took place. There was no noticeable action until 160°, although phenyl isocyanate was undoubtedly being evolved at a temperature somewhat below that.

**Analysis.** Subs., 0.1788:  $K_2SO_4$ , 0.0538. Calc. for  $C_{12}H_9O_2NSK$ : K, 13.70. Found: 13.50.

**Silver Salt.**—When silver nitrate, in water solution, was added to a solution of the potassium salt in water, a voluminous white precipitate of the silver salt resulted. It blackened near 165°.

**Analysis.** Subs., 0.0897; Ag, 0.0274. Calc. for  $C_{12}H_9O_2NSAg$ : Ag, 30.47. Found: 30.54.

### Summary.

An interpretation of the mechanism of the Beckmann rearrangement has been proposed, based upon the modern conception of chemical bonds

and electrons. The transfer of electrons for all stages in the process has been pictured in a detailed manner.

The following hypothesis has been advanced: the relative ease of rearrangements of the Beckmann type is dependent upon the tendency for the radical R in the univalent nitrogen derivative, *e. g.*, (R.CO.N), to exist as a free radical.

The hypothesis was tested successfully with the sodium and the potassium salts of the acyl esters both of diphenylacethydroxamic acid and of triphenylacethydroxamic acid. Rearrangement of the salts in solution was found to be more reliable for purposes of comparison than rearrangement of the solid salts. In agreement with the hypothesis, the relative ease of rearrangement was greater with triphenylacethydroxamic acid derivatives than with the similar compounds in the diphenyl series. When water solutions of the salts in the triphenyl series were heated, the product of rearrangement was triphenylmethyl isocyanate, and not *sym.* bi-triphenylmethyl urea. This is a singular fact. The phenomenon of chromo-isomerism was displayed by the silver salts of the diphenyl series, as well as those of the triphenyl series.

Diphenyl ketene and hydroxylamine were found to react readily in a neutral solvent to form diphenylacethydroxamic acid. Modifications of this new reaction between ketenes and hydroxylamine, or substituted hydroxylamines, should be valuable in future synthetic work.

The properties of pyromucyl-hydroxamic acid, and of  $\alpha$ -thenhydroxamic acid have been determined. The latter resembles benzhydroxamic acid very closely. The former is similar to benzhydroxamic acid in many respects, but its derivatives differ materially in rearrangement. These two compounds, which are representatives of the furane and of the thiophene types, prepare the way for further investigations of heterocyclic hydroxamic acids.

PRINCETON, NEW JERSEY.



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

ACTION OF ARSENIUS CHLORIDE ON ANILINE.<sup>1</sup>

BY JOHN H. SCHMIDT.

Received July 14, 1921.

## Introduction.

The action of arsenious chloride upon aniline has been studied by a number of investigators, each of whom has obtained different results. The reaction was first investigated by Schiff,<sup>2</sup> who described compounds resulting from the direct action of arsenious chloride and iodide on aniline, to which he assigned the formulas,  $\text{As} \equiv (\text{NHC}_6\text{H}_5\text{HCl})_3$  and  $\text{As} \equiv (\text{NHC}_6\text{H}_5\text{HI})_3$ . Leeds<sup>3</sup> obtained somewhat similar results, while Landau<sup>4</sup> allowed arsenious chloride to react with aniline in benzene solution and obtained a compound to which he assigned the formula:  $\text{AsCl}_3 + 4(\text{C}_6\text{H}_5\text{NH}_2) + \text{H}_2\text{O}$ . Anschütz and Meyer<sup>5</sup> were unable to obtain a compound corresponding to the one described by Schiff, and state that the third halogen of arsenic halide is not replaceable by aniline. They also show that the compounds described by Landau were probably nothing more than impure mixtures. They isolated two compounds, however, to which they assign the formulas,  $\text{As}(\text{NHC}_6\text{H}_5)_2\text{Cl}_2$  and  $\text{As}(\text{NHC}_6\text{H}_5)_2\text{Cl}$ , and the corresponding arsenanilide dimethyl and diethyl esters.

More recently Morgan and Micklethwait<sup>6</sup> describe a condensation product obtained by adding arsenious chloride to aniline in benzene solution. They assign to this compound either of the two formulas,  $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{As}(\text{C}_6\text{H}_4\text{NH}_2)_2$ , or  $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{As}(\text{NHC}_6\text{H}_5)_2\text{C}_6\text{H}_5\text{NH}_2$ .

Substituted anilines have been more thoroughly investigated. Michaelis and Rabinerson<sup>7</sup> found that dimethyl- and diethyl-aniline contain a reactive hydrogen atom readily replaceable by an arsenic radical, and in this manner prepared a number of substituted arsanilic acids.

In this research a study has been made of the action of arsenious chloride on aniline in *n*-heptane solution, with the result that a yellow granular substance was obtained, which could be purified by vacuum sublimation. This was apparently similar to Schiff's compound, except that it had a much higher melting point. The product showed interesting decomposition reactions, being transformed readily by heating it, either alone or preferably with an excess of aniline, into cyclic arsenic compounds.<sup>8</sup> The

<sup>1</sup> Abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin.

<sup>2</sup> Schiff, *Compt. rend.*, 56, 268, 1095 (1863).

<sup>3</sup> Leeds, *THIS JOURNAL*, 3, 134 (1882).

<sup>4</sup> Landau, *Inaug. Diss.*, Berlin, 1888.

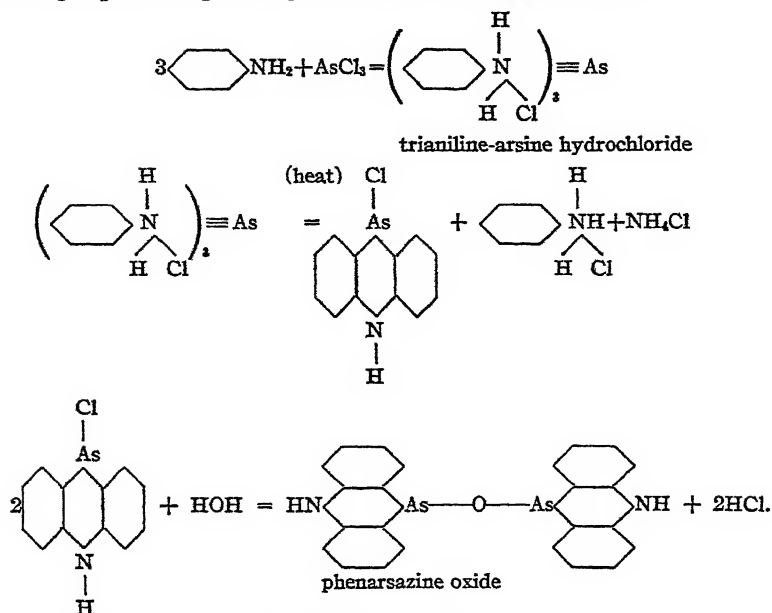
<sup>5</sup> Anschütz and Meyer, *Ann.*, 261, 279 (1890).

<sup>6</sup> Morgan and Micklethwait, *J. Chem. Soc.*, 45, 1473 (1909).

<sup>7</sup> Michaelis and Rabinerson, *Ann.*, 270, 139 (1892).

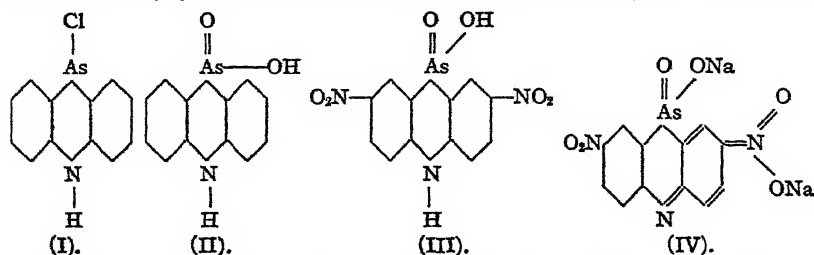
<sup>8</sup> This work was completed previous to the publication by Wieland and Rheinheimer, *Ann.*, 423, 1 (1921), on the preparation of similar condensation products obtained by the condensation of diphenylamine and arsenious chloride.

following equations probably indicate this transformation.

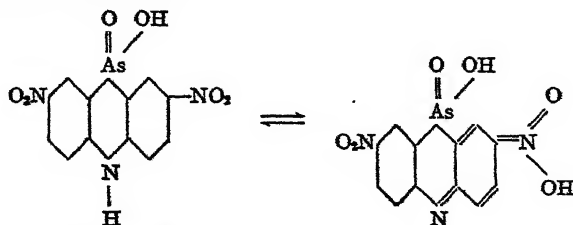


Chloro-phenarsazine, to which Formula I has been assigned, has been previously prepared<sup>9</sup> by the action of arsenious chloride on diphenylamine.

Phenarsazine oxide was found to yield on oxidation the corresponding arsonic acid, (II) and on nitration a dinitro-arsonic acid (III). The latter



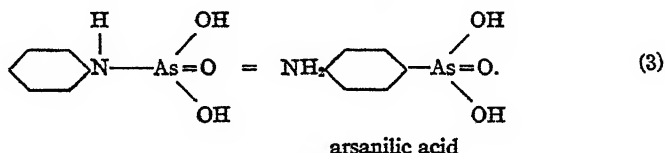
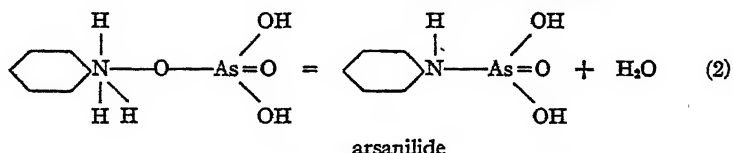
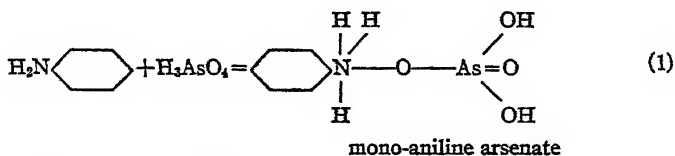
compound may evidently exist in two tautomeric modifications, which may be represented as follows.



<sup>9</sup> Ger. pat. 281,049; *Centr.*, 86, 72 (1915).

This would satisfactorily explain the intense red color of alkaline solutions of the nitro compound. Further proof for this assumption has been obtained by the isolation of a di-sodium salt (IV) of the nitro derivative.

The study of the reaction of arsenious chloride and aniline was undertaken originally in an attempt to prepare "arsanilide," a substance which should be formed as an intermediate in the preparation of arsanilic acid by the reaction of aniline and arsenic acid according to the following equations.



The preparation of both a mono-aniline and di-aniline arsenate was easily accomplished, but it was found impossible to transform the former into an "arsanilide."

### Experimental.

**Trianiline-arsine Hydrochloride.**—The heptane<sup>10</sup> used was purified according to the method of Sher<sup>11</sup> and dried over sodium. The aniline used was twice distilled and dried over sodium hydroxide. The arsenious chloride was a pure commercial material and not further purified.

Nine cc. of arsenious chloride (18 g. or  $\frac{1}{3}$  mol) was added to 100 cc. of heptane contained in a large test-tube fitted with a mechanical stirrer and dropping funnel. The test-tube was kept well surrounded with ice. To the heptane solution of arsenious chloride 31 cc. of aniline ( $\frac{1}{3}$  mol plus a slight excess) was slowly added with stirring. Immediate precipitation of a yellow granular compound occurred. After the complete addition of the aniline, stirring was continued for 15 minutes more and the reaction mixture then rapidly filtered with suction. The crude product was dried in a vacuum at 100°, since it holds heptane very tenaciously.

The ease with which the compound underwent decomposition and its insolubility in the common inert solvents (acetone, ether, benzene, and chloroform) made it extremely difficult to purify. Distillation in a vacuum was impractical, since the dis-

<sup>10</sup> The heptane was kindly furnished by Dr. Kremers, Director of the Pharmacy Department, University of Wisconsin.

<sup>11</sup> Sher<sup>11</sup>, *Thesis*, University of Wisconsin, 1918.

tillate adheres so tenaciously to the receiver that it was often necessary to break the flask to obtain the product. Purification was finally effected by vacuum sublimation.

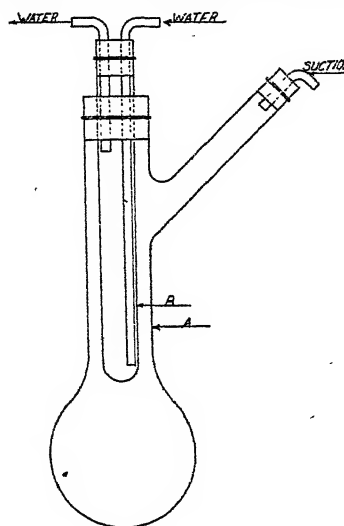


Fig. 1.

An apparatus was designed for this purpose, which is shown in Fig. 1. It consisted of a Beckmann boiling-point apparatus, A, in which a water-cooled test-tube, B, was inserted to serve as a condenser. The substance to be sublimed was placed in the outer flask, A, which was heated by a metal bath. The sublimate condensed on tube B to which it adhered firmly and was easily removed without loss.

The purified compound is a light yellow, crystalline solid melting with some decomposition at 148–150°, which is 60° higher than the melting point assigned to the compound isolated by Schiff. It is readily decomposed by water and absolute alcohol, dissolving in them to a clear solution when heated, but on cooling a mixture of arsenious oxide and aniline hydrochloride crystallizes out. The product undergoes oxidation on exposure to air and, unless immediately analyzed, gives somewhat low results for arsenic. Arsenic was determined

by the method of Little, Cahen and Morgan,<sup>12</sup> chlorine by Stepanow's<sup>13</sup> method, and nitrogen by the Kjeldahl-Gunning method.

**Analyses.** Calc. for  $C_{13}H_{21}N_3Cl_2As$ : N, 9.13; Cl, 23.10; As, 16.30. Found: N, 9.25, 9.21; Cl, 23.15, 23.00; As, 15.74, 15.75, 15.55.

**Phenarsazine Oxide.**—Five hundred cc. of dry redistilled aniline was placed in a 1-liter flask fitted with a dropping funnel and a reflux air condenser; 180 g. or 90 cc. of arsenious chloride was then added through the dropping funnel, a yellow precipitate of tri-aniline arsine hydrochloride being formed. On heating, the precipitate dissolved, the solution slowly darkening until finally it was deep purple in color. The temperature was slowly raised to the boiling point and boiling continued for 72 hours. While still hot the solution was poured into a 3-liter flask and 500 cc. of hot water carefully added. On cooling, the solution was made alkaline with sodium carbonate and the excess of aniline distilled with steam, the distillate being strongly alkaline, due to the ammonia formed in the reaction. The solution remaining in the flask was filtered away from the dark green powder which was washed several times with hot water, then with acetone and then again with hot water. This effectually removed the greater part of the impurities formed with the compound. For final purification it was recrystallized thrice from 80% acetic acid. When pure the compound was a pale yellow, crystalline solid, melting above 300°. The dry powder was extremely irritating to the membranes of the nose and mouth. The oxide was insoluble in alcohol, acetone, benzene, chloroform, ether, alkalis and dilute acids, but soluble in acetic acid and conc. sulfuric acid. The solution in sulfuric acid was deep purple in color, turning green upon addition of a trace of nitric acid. Water precipitated the original compound from its sulfuric acid solution. Yield of crude product, 70%. Analysis gave the following results, the arsenic and nitrogen being determined as in the previous experi-

<sup>12</sup> Little, Cahen and Morgan, *J. Chem. Soc.*, 109, 1356 (1916).

<sup>13</sup> Stepanow, *Ber.*, 39, 4056 (1906).

ment, while combustion of the substance for determination of carbon and hydrogen was carried out in a tube filled with granulated lead chromate.

*Analyses.* Calc. for  $C_{12}H_{11}ON_2As_2$ : C, 57.60; H, 3.60; N, 5.60; As, 30.00. Found: C, 58.2, 58.09; H, 3.85, 3.57; N, 5.70, 5.74; As, 30.19, 30.05.

**Phenazarsonic Acid.**—Five g. of pure phenarsazine oxide was added to 100 cc. of water and 20 cc. of 15% sodium hydroxide solution. Ten to 20 cc. of perhydrol (30% hydrogen peroxide) was added and the mixture shaken and warmed until complete solution took place. The excess of hydrogen peroxide was decomposed by boiling, the solution filtered, cooled and acidified with acetic acid, the phenazarsonic acid being precipitated out. It was recrystallized from 50% acetic acid. It should be noted that pure phenarsazine oxide must be used, since certain impurities in the crude product completely prevent its oxidation by hydrogen peroxide. The pure product was a very pale yellow, crystalline solid, melting above  $300^\circ$ ; yield 85%. It was readily soluble in dilute alkalis, insoluble in acetone, ether and alcohol.

*Analyses.* Calc. for  $C_{12}H_{10}O_2NAs$ : C, 52.36; H, 3.63; N, 5.09; As, 27.27. Found: C, 52.87, 52.37; H, 3.63, 3.74; N, 4.30, 4.83; As, 26.81, 26.93.

**Dinitro-phenazarsonic Acid.**—Five g. of pure phenarsazine oxide was heated under a reflux condenser with a mixture of 300 cc. of nitric acid (1:2) and 40 cc. of acetic acid until complete solution took place. The hot solution was filtered through glass wool into 2 liters of cold water, the nitro derivative being immediately precipitated. The crude product was purified by dissolving it in hot dil. ammonium hydroxide, filtering and reprecipitating the nitro compound with dil. hydrochloric acid; yield 80%. The pure product was a bright yellow powder which decomposed with a bright flash on heating. It was readily soluble in alkalis, forming a deep red solution, but sparingly soluble in water and alcohol. Analysis gave the following results, the nitrogen being determined by the modified Kjeldahl method for determining nitrogen in nitro compounds. Combustion of the substance was very difficult due to its explosive nature, the difficulty being finally overcome by distributing the substance in small portions along the boat and using extreme care in heating it.

*Analyses.* Calc. for  $C_{12}H_8O_6N_2As$ : C, 39.45; H, 2.19; N, 11.50; As, 20.54. Found: C, 39.92, 39.89, 39.40; H, 2.42, 2.44, 2.21; N, 11.8, 11.5; As, 20.16, 20.20.

**The Sodium Salt of Dinitro-phenazarsonic Acid.**—Two g. of the nitro compound was dissolved in the required amount of 0.025 *N* alkali to form the disodium salt. The solution was concentrated to a small volume on the water-bath, and on cooling the sodium salt crystallized out. It was recrystallized twice from alcohol, the pure product being a yellow crystalline solid, readily soluble in water, soluble in hot alcohol to form a bright red solution, but less soluble in the cold.

*Analyses.* Calc. for  $C_{12}H_6O_6N_2AsNa_2$ : As, 18.34. Found: 18.63, 18.35.

**Mono-aniline Salt of Arsenic Acid.**—This was prepared by dissolving redistilled aniline in alcohol, adding to it an excess of sirupy arsenic acid and warming until the aniline arsenate was in solution. On cooling, the mono-aniline salt crystallized in fine pearly leaflets. It was twice recrystallized from alcohol; m. p.,  $147-148^\circ$ . Arsenic was determined by Ewins<sup>14</sup> method and nitrogen by the Kjeldahl-Gunning method.

*Analyses.* Calc. for  $C_6H_7O_4NAs$ : N, 5.95; As, 31.91. Found: N, 6.22, 6.23; As, 31.67, 31.89.

Unsuccessful attempts were made to convert this salt into an "arsanilide" by heating it in either nitrobenzene, chlorobenzene or xylene. The use of dehydrating agents such as calcium oxide and copper sulfate also failed to give the desired result.

<sup>14</sup> Ewins, *J. Chem. Soc.*, 109, 1356 (1916).

**Di-aniline Salt of Arsenic Acid.**—This was prepared by dissolving sirupy arsenic acid in alcohol, adding to it an excess of aniline and warming until the di-aniline salt was in solution. On cooling, it crystallized in pearly leaflets; *m. p.*, 143°.

*Analyses.* Calc. for  $C_{12}H_{17}O_4N_2As$ : N, 8.53; As, 22.86. Found: N, 8.11, 8.10; As, 23.23, 23.32.

### Summary.

1. The reaction between aniline and arsenious chloride has been studied and a new method for the preparation of secondary arsonic acid derivatives devised.

2. Tri-aniline-arsine hydrochloride has been prepared in a pure state and its properties described.

3. Several new compounds, phenarsazine oxide, phenazine-arsonic acid, dinitro-phenazine-arsonic acid, and disodium dinitro-phenazine-arsonic acid have been prepared and their methods of preparation and properties described.

4. A new vacuum sublimation apparatus has been described.

5. Directions for the preparation of mono-aniline and di-aniline salts of arsenic acid have been given.

The writer wishes to express his gratitude to Professor Richard Fischer, under whose direction this work has been carried out, and also to Professors Loevenhart and Kremers, for their interest in this research.

MADISON, WISCONSIN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 374.]

## EFFECT OF CERTAIN ANTISEPTICS UPON THE ACTIVITY OF AMYLASES.

BY H. C. SHERMAN AND MARGUERITE WAYMAN.

Received July 22, 1921.

In experimental studies of enzyme action, antiseptics are frequently used to prevent or suppress any activities of microorganisms. It is obviously important to know as definitely as possible whether antiseptics can be thus used without influence upon the activity of the enzyme which it is desired to study; and furthermore we may hope that a systematic determination of the behavior of enzymes toward antiseptics of different types may ultimately throw light upon the chemical nature of the enzymes themselves and the discussion of enzyme dispersions in terms of colloid chemistry.

The experiments here recorded have to do with the influence of toluene, formaldehyde, and copper sulfate upon amylases of both animal and vegetable origin and when tested in both natural and purified form. The literature affords many statements of a general nature regarding the relation of antiseptics to enzyme action, usually giving the impression that

those of the type of toluene or chloroform have little if any influence upon enzymes while such antiseptics as formaldehyde and copper sulfate are more likely to prove injurious. Precise statements accompanied by experimental evidence appear to be few.

Chittenden and Painter<sup>1</sup> in the course of a study of the effects of numerous salts upon saliva, found copper sulfate to be very injurious to its starch-digesting action.

Grützner and Wachsmann<sup>2</sup> reported that ether, chloroform and thymol retard the action of pancreatic amylase, chloroform being the most destructive of the three.

Kopaczewski<sup>3</sup> could observe no effect of chloroform or toluene in a concentration of 0.1% upon the action of takadiastase, which action, however, was prevented by 1.0% formaldehyde.

Myers and Scott<sup>4</sup> found salivary amylase to be relatively stable in the presence of chloroform, toluene or thymol, toluene appearing to preserve the activity of the enzyme the best of these three antiseptics.

Bokorny<sup>5</sup> reported that maltase was injured by 0.1%, and destroyed by 1% of formaldehyde.

**Materials and Methods.**—The amylase preparations employed in this investigation consisted of: (1) commercial pancreatin, Lab. No. 8; (2) purified pancreatic amylase, preparations T-8-B, T-18-A, T-18-B made as described in a previous paper<sup>6</sup> and having amylolytic powers of about 3000 according to the method and scale in use in this laboratory since 1910;<sup>7</sup> (3) human saliva as secreted; (4) malt extract; (5) purified malt amylase, Lab. No. 151, amylolytic power<sup>7</sup> 1274; (6) takadiastase, commercial; (7) the purified amylase of *Aspergillus oryzae* prepared from takadiastase and having about 30 times its amylolytic power. We are indebted to Parke, Davis and Company for the pancreatin and takadiastase used.

The starch, water, and other materials employed were purified as described in previous papers from this laboratory.

The purest obtainable chloroform, toluene, copper sulfate, and formaldehyde were employed. The percentage strength of the last substance was determined by the peroxide method.

The plan of experimentation was to allow a suitable amount of an amylase solution to act upon 100 cc. of 2 % starch paste with and without the antiseptic to be tested in the presence of suitable "activating" salts for 30 minutes at 40° in the same manner as for the determination of diastatic power by the gravimetric method of Sherman, Kendall and Clark,<sup>7</sup> the reducing

<sup>1</sup> Chittenden and Painter, "Studies from the Yale Laboratory of Physiological Chemistry," 1-3, p. 55 (1884-8).

<sup>2</sup> Grützner and Wachsmann, *Pflüger's Archiv*, 91, 195-207 (1902); *J. Chem. Soc.*, 82, II, 614 (1902).

<sup>3</sup> Kopaczewski, *Biochem. Z.*, 44, 351 (1912).

<sup>4</sup> Myers and Scott, *THIS JOURNAL*, 40, 1713 (1918).

<sup>5</sup> Bokorny, *Biochem. Z.*, 94, 71 (1919).

<sup>6</sup> Sherman and Neun, *THIS JOURNAL*, 41, 1855 (1919).

<sup>7</sup> Sherman, Kendall and Clark, *ibid.*, 32, 1082 (1910).

sugar formed by the action of the amylase upon the starch being estimated by heating with an excess of Fehling solution and the result expressed in terms of mg. of cuprous oxide reduced, allowance being made for the reduction resulting from the starch alone or the starch plus antiseptics as determined by blank tests.

### Experiments with Toluene.

Of the antiseptics of the "lipoid solvent" type, the ones most commonly used in enzyme work are chloroform and toluene. Preliminary experiments indicated that chloroform at a concentration of 0.0000124 *M* measurably diminished the action of purified pancreatic or malt amylase but not of a simple malt extract. Chloroform, however, did not lend itself readily to experimentation by the method here used because of its reducing effect upon Fehling solution. Since chloroform and toluene are so largely used interchangeably in work with enzymes and toluene does not appreciably influence the reduction of Fehling solution, it was chosen in preference to chloroform for the following series of experiments. In testing its influence upon the enzyme, 5 cc. of toluene was shaken with the 100 cc. of digestion mixture and the insoluble surplus allowed to remain upon the surface of the substrate.

The results of parallel determinations with and without toluene are shown in Table I.

TABLE I.  
EFFECT OF TOLUENE UPON VARIOUS AMYLASES.

Enzyme.			Reduction of $\text{Cu}_2\text{O}$ .		Loss of Activity.
Kind.	Amount. Mg.	No $\text{C}_7\text{H}_8$ . Mg.	5 cc. $\text{C}_7\text{H}_8$ . Mg.		%.
Commercial pancreatin, No. 8....	0.96	333.6	331.8		?
Purified pancreatic amylase, No.					
T 18A .....	0.05	200.7	191.0		5
Saliva.....	0.06 cc.	201.7	194.5		4
Malt extract.....	0.035 cc.	238.4	216.0		9
Purified malt amylase, No. 151..	0.15	329.6	304.7		8
Commercial takadiastase, No. 7.	5	308.6	304.4		1
Aspergillus amylase, No. 22b ...	0.25	293.4	285.9		3

From these results it appears that commercial pancreatin and takadiastase were influenced to only a negligible extent if at all by the saturation of the digestion mixture with toluene, while saliva, malt extract and the purified amylase preparations were measurably inhibited in their action, but not inactivated to any very serious extent. This is in accordance with the results of a previous series of experiments carried out by Miss Jennie A. Walker and one of us, in which the action of purified malt amylase was repeatedly found to be slightly diminished by the presence of toluene, but to an extent little if any greater than the variations to be expected between duplicate experiments with such enzyme preparations.





able loss of activity of commercial pancreatin and that the loss increased regularly with the concentration of the formaldehyde. Because of the reduction of Fehling's solution by the formaldehyde itself, it was not feasible to carry these experiments to a higher concentration than approximately 0.00017 *M*.

In order to see whether the concentration of the enzyme solution made any difference in the amount of inhibition caused by 10 cc. of formaldehyde solution, 0.4 cc., 0.6 cc., and 0.8 cc. of the enzyme solution were used. The results are given in Table III.

TABLE III.

EFFECT OF FORMALDEHYDE UPON VARIOUS CONCENTRATIONS OF PANCREATIN.

Cc.	Pancreatin. Mg.	Reduction of $\text{Cu}_2\text{O}$ .		10 cc. (0.000116 <i>M</i> ). Mg.	Loss of Activity. %.
		No HCHO.	Mg.		
0.4	0.48	132.3		110.0	17
0.6	0.72	204.4		166.8	18
0.8	0.96	269.4		218.5	19

According to these results, it made practically no difference in the percentage of retardation whether 0.48 mg., 0.72 mg., or 0.96 mg. was used with 2% starch paste in the presence of 10 cc. of formaldehyde solution.

To see whether the concentration of starch affected the result, 1%, 2%, and 4% starch pastes were used with 0.96 mg. of commercial pancreatin in the presence and absence of formaldehyde. The results are shown in Table IV.

TABLE IV.

EFFECT OF FORMALDEHYDE UPON THE ACTION OF PANCREATIN ON DIFFERENT CONCENTRATIONS OF STARCH.

Conc. of Starch. %.	Reduction of $\text{Cu}_2\text{O}$ .		Loss of Activity. %.
	No HCHO. Mg.	10 cc. (0.000116 <i>M</i> ). Mg.	
1	222.8	173.9	22
2	259.1	208.5	20
4	277.5	228.2	18

The percentage of destruction did not vary much no matter whether 1%, 2% or 4% starch was used.

From Tables II to IV it can be seen that the percentage loss of activity of commercial pancreatin depends not upon the concentration of the enzyme or the concentration of the substrate, but only upon the concentration of the antiseptic.

### Experiments with Copper Sulfate.

A 0.00056 *M* copper sulfate solution was prepared, and 5 cc., 10 cc. and 15 cc. of this solution used in the experiments. The results are given in Table V.

TABLE V.  
EFFECT OF COPPER SULFATE UPON VARIOUS AMYLASES.

Kind.	Enzyme.	Amount.	Cu <sub>2</sub> O.				Loss of Activity.			
			No CuSO <sub>4</sub> .	5 cc. CuSO <sub>4</sub> (0.000028 M)	10 cc. CuSO <sub>4</sub> (0.000056 M)	15 cc. CuSO <sub>4</sub> (0.000084 M)	5 cc. CuSO <sub>4</sub> (0.000028 M)	10 cc. CuSO <sub>4</sub> (0.000056 M)	15 cc. CuSO <sub>4</sub> (0.000084 M)	
			Mg.	Mg.	Mg.	Mg.	%.	%.	%.	
Comm. pancreatin, No. 8.....		0.96	278.7	82.7	71.2	62.8	70	74	77	
Pur. pancreatic amylase, No. T 18B.....		0.07	206.6	51.4	48.0	43.0	75	77	79	
Saliva.....		0.66 cc.	267.1	170.3	167.3	166.8	36	37	38	
Malt extract.....		0.035 cc.	245.9	215.6	189.1	166.5	12	23	32	
Pur. malt amylase, No. 151 ....		0.15	342.6	322.2	306.8	296.2	6	10	14	
Comm. takadiastase, No. 7.....		5.00	303.8	291.5	277.6	266.3	4	9	12	
Aspergillus amylase, No. 22b...		0.25	279.0	257.9	241.9	232.0	8	13	17	

The results in Table V show that all of the amylases studied were affected by from 0.000028 *M* to 0.000084 *M* copper sulfate. The pancreatic and salivary amylases were affected considerably more than malt amylase and takadiastase.

Assuming that the iso-electric points of the amylase proteins are in the range of other proteins previously reported by Loeb and others, namely in the vicinity of  $C_H^+ 10^{-5}$ , and since the activity of the pancreatic amylase was measured in the presence of electrolytes at a reaction of about  $C_H^+ 10^{-7}$  while the reaction of the substrate solutions in the cases of malt amylase and takadiastase was about  $C_H^+ 10^{-4.5}$ , it would appear that the greater destruction of pancreatic amylase may be due to the formation of insoluble copper-proteinates<sup>3</sup> which would form at the hydrogen-ion concentration of the substrate solution as prepared for the pancreatic, but not as prepared for the malt and aspergillus amylases. We hope soon to study the iso-electric points of some of these amylase preparations.

Saliva was affected only about half as much as was the pancreatic amylase. This may be due to the presence in the saliva of a relatively large amount of other protein which would tend to protect the amylase by removing copper in the manner suggested above.

The results of a second series of experiments with a new solution of copper sulfate, used in such amounts as to give a wider range of final concentrations than in those above described, are shown in Table VI.

It may be seen from Table VI that in the presence of exceedingly minute amounts of copper sulfate its inhibitory effect is much more pronounced in the case of the pancreatic than of the malt amylase. In all cases the percentage loss of activity increases with increasing concentration of copper. Purified pancreatic amylase was tested with somewhat larger amounts

<sup>3</sup> Loeb, *J. Gen. Physiol.* 1918-19, *passim*.

TABLE VI.  
EFFECT OF COPPER SULFATE UPON CERTAIN AMYLASES.

Kind.	Enzyme.	Amount.	Cu <sub>2</sub> O.				Loss of Activity.		
			No CuSO <sub>4</sub> .	1 cc. CuSO <sub>4</sub> (0.00006 M).	10 cc. CuSO <sub>4</sub> (0.00006 M).	50 cc. CuSO <sub>4</sub> (0.0003 M).	1 cc. CuSO <sub>4</sub> (0.00006 M).	10 cc. CuSO <sub>4</sub> (0.00006 M).	50 cc. CuSO <sub>4</sub> (0.0003 M).
		Mg.	Mg.	Mg.	Mg.	Mg.	%.	%.	%.
Comm. pancreatin, No. 8.....		0.96	264.1	135.5	66.0	43.7	49	75	83
Pur. pancreatic amylase, No. T 18B.....		0.07	298.3	122.4	71.7	41.6	59	76	86
Saliva.....		0.06 cc.	183.1	131.4	116.1	105.6	28	37	42
Malt extract.....		0.035 cc.	263.1	257.4	197.9	92.1	2	25	65
Pur. malt amylase, No. 151.....		0.15	308.4	308.2	279.9	199.5	..	9	35

than in the above experiments with the result that copper sulfate at 0.00042 *M* was found to deprive it of 89% of its activity; and at 0.00054 *M*, 92% of the activity was lost.

Experiments with various concentrations of enzyme (pancreatin) and of starch, similar to those described under formaldehyde, were performed with copper sulfate.

The results are shown in Tables VII and VIII.

TABLE VII.  
EFFECT OF COPPER SULFATE WITH VARIOUS CONCENTRATIONS OF PANCREATIN.

Cc. Pancreatin.	Mg.	Reduction of Cu <sub>2</sub> O.		Loss of Activity.
		No CuSO <sub>4</sub> .	10 cc. (0.00006 M).	
		Mg.	Mg.	%.
0.4	0.48	140.5	36.3	74
0.6	0.72	204.8	55.7	73
0.8	0.96	280.9	74.5	74

TABLE VIII.  
EFFECT OF COPPER SULFATE UPON THE ACTION OF PANCREATIN ON STARCH AT DIFFERENT CONCENTRATIONS.

Conc. of Starch.	Reduction of Cu <sub>2</sub> O.		Loss of Activity.
	No CuSO <sub>4</sub> .	10 cc. (0.00006 M).	
%.	Mg.	Mg.	%.
1	240.8	71.1	70
2	276.8	79.0	71
4	290.3	88.8	69

From Tables VII and VIII it will be observed that the percentage of loss of activity of pancreatin is practically unaffected by a change in enzyme concentration or by a change in the starch concentration. It is not the ratio of antiseptic to enzyme or of antiseptic to substrate, but the ratio of antiseptic to water which determines the activity of the amylase.

### Summary.

Low concentrations of chloroform did not affect commercial pancreatin or malt extract, but did affect the purified preparations of these amylases.

Toluene had very little influence upon the activities of the amylases either in their natural or purified condition.

Commercial pancreatin, purified pancreatic amylase, saliva, malt extract, purified malt amylase, commercial takadiastase, and the purified amylase of *Aspergillus oryzae* were all injured by formaldehyde even in small amounts. Takadiastase was the least, and purified pancreatic amylase the most, affected. The percentage of loss of the enzyme action increased in all cases with increasing concentration of formaldehyde.

A very low concentration of formaldehyde (0.0000116 *M*) gave a 3% destruction of the activity of commercial pancreatin.

All of the enzymes studied were very sensitive to copper sulfate. Pancreatic amylase was much more sensitive than any of the others. Most of the enzymes were injured by as low a concentration of copper sulfate as 0.000006 *M*. Almost complete destruction of the activity of purified pancreatic amylase was caused by 0.00054 *M* copper sulfate. The inhibiting effect of copper sulfate on the activity of amylases increased with increasing concentration of copper sulfate.

The percentage loss of enzyme action due to formaldehyde and to copper sulfate solution did not depend upon the ratio of antiseptic to enzyme or of antiseptic to substrate, but upon the ratio of antiseptic to water, or the concentration of the antiseptic in the system.

The results demonstrate the need of attention to the possible effects of antiseptic upon enzyme in cases in which antiseptics are used to suppress microorganisms in studies of enzyme activity.

The much greater sensitiveness of the amylases to formaldehyde and copper sulfate than to toluene is of further interest in connection with the problem of the protein nature of these enzymes.

We are indebted to the Carnegie Institution of Washington for the use of enzyme preparations which had been purified in connection with work done under the auspices of the Institution.

NEW YORK CITY.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 375.]

## THE INFLUENCE OF CERTAIN AMINO ACIDS UPON THE ENZYMIC HYDROLYSIS OF STARCH.

BY H. C. SHERMAN AND FLORENCE WALKER.

Received July 22, 1921.

Our experiments on the influence of amino acids upon the rate of hydrolysis of starch by different enzymes, begun with the study of asparagine and aspartic acid,<sup>1</sup> have been extended to glycine, alanine, tyrosine and phenylalanine. Essentially the same experimental methods have been employed as in our work with asparagine and aspartic acid. In the experiments described below, however, "soluble" starch, prepared by the Lintner

<sup>1</sup> Sherman and Walker, *THIS JOURNAL*, **41**, 1867 (1919).

method and further purified by washing 9 times with ordinary distilled and 6 times with specially purified thrice distilled water, has in all cases been used as substrate. The amino acids here used were imported. The amylase preparations and other enzyme-containing materials tested were (1) pancreatic amylase preparations Nos. 58, 59, 60, 77B and 81B, (2) commercial pancreatin No. 8, (3) malt amylase preparation No. 155, (4) malt extract, (5) aspergillus amylase preparations Nos. 22, 22b, and 23, (6) commercial takadiastase, and (7) fresh saliva. Thrice distilled water was used for making starch dispersions, solutions of activators, enzymes, etc., and for rinsing all glassware.

**Method.**—The method<sup>2</sup> of testing the influence of the amino acids is briefly as follows. An amount of air-dry starch equivalent to the required amount of anhydrous material is weighed out, mixed with a little cold water, dispersed by pouring into boiling water (about 80 cc. per g. of starch) and boiled for about 3 minutes. This is transferred to 100cc. cylinders, neutralized with 0.01 *N* sodium hydroxide solution and the salts most favorable for the action of the amylase<sup>3</sup> added. The dispersions are then made up to 100 cc. so that the concentration of starch is exactly 1%, mixed thoroughly by stirring and placed in the 40° bath to reach the desired temperature. In the meantime, the enzyme solution is prepared and the required amount pipetted into dry flasks. The starch dispersions are then poured into the flasks containing the enzyme at intervals of 15 seconds and the flasks placed in the 40° bath. At the end of 30 minutes, enzymic action is stopped by pouring 50 cc. of Fehling solution into the digestion mixtures, at intervals of 15 seconds and in the same order in which the starch was poured on the enzyme. The amount of reducing sugar formed is determined by immersing the flasks in a boiling water bath for 15 minutes. The cuprous oxide is filtered into weighed Gooch crucibles, washed with hot water, alcohol and ether, dried at 100°, and weighed. Glycine and alanine being quite soluble were dissolved in a small volume of water and added to the starch paste, after it was poured into the cylinders and before being made up to volume. Since tyrosine and phenylalanine are difficultly soluble, the amount of each used was added to the water in which the starch was dispersed and boiled with it. To show whether this variation in procedure affected the action of the amino acid on the enzyme, digestions were carried out in which equal amounts of asparagine were added before boiling in some cases and after cooling in others. Activation due to asparagine was the same in both cases. The same test was made with aspartic acid with the same result.

<sup>2</sup> Sherman, Kendall and Clark, *THIS JOURNAL*, 32, 1082 (1910).

<sup>3</sup> Sherman, Thomas and Baldwin, *ibid.*, 41, 231 (1919). Pending further investigation the substrate is prepared in the same manner for the action of saliva as for pancreatic amylase.

In these experiments the amino acids were made neutral to rosolic acid with 0.01 *N* sodium hydroxide solution.

### Measurement of the Influence of Different Amino Acids.

Tables I-IV show the influence of carefully neutralized glycine, alanine, tyrosine and phenylalanine, added separately and in combination with a second amino acid, upon the rate of hydrolysis of "soluble starch" by different enzymes. The reducing sugar formed by enzymic hydrolysis is chiefly maltose, but since small amounts of glucose may also be present the results are stated in terms of the weight of cuprous oxide resulting from the reduction of the Fehling solution by the sugar or sugars present. The amounts of enzyme used in the experiments were so regulated as to result in the transformation of about 1/5 of the starch into sugar.

TABLE I.

EFFECT OF GLYCINE AND GLYCINE PLUS ASPARTIC ACID ON THE ENZYMIC HYDROLYSIS OF LINTNER SOLUBLE STARCH.

Amino acid.			Cuprous oxide.					
Glycine. Mg.	Aspartic acid. Mg.	Purified pancreatic amylase (No. 59). Mg.	Commercial pancreatin (No. 8). Mg.	Saliva. Mg.	Purified malt amylase (No. 155). Mg.	Malt extract. Mg.	Aspergillus amylase (No. 23). Mg.	Commercial takadiastase (No. 7). Mg.
None	None	246	227	316	260	277	222	292
50		280	243	334	270	286	226	292
100		284	245	341	273	283	224	292
None	50	279	242	344	269	280	223	289
50	50	279	247	334	268	281	224	292
Activation due to glycine =		38	18	25	13	9	4	0

TABLE II.

EFFECT OF ALANINE AND ALANINE PLUS GLYCINE ON THE ENZYMIC HYDROLYSIS OF LINTNER SOLUBLE STARCH.

Amino acid.			Cuprous oxide.					
Alanine. Mg.	Glycine. Mg.	Purified pancreatic amylase (No. 58). Mg.	Commercial pancreatin (No. 8). Mg.	Saliva. Mg.	Purified malt amylase (No. 155). Mg.	Malt extract. Mg.	Aspergillus amylase (No. 22b). Mg.	Commercial takadiastase (No. 7). Mg.
None	None	273	281	319	285	248	272	279
50		310	293	339	295	251	279	282
100		318	301	352	301	257	287	290
None	50	320	300	355	299	249	277	280
50	50	318	296	360	305	256	284	286
25	25	317	298	351	299	250	273	283
Activation due to alanine		42	20	33	16	9	15	11

TABLE III.  
EFFECT OF TYROSINE AND TYROSINE PLUS ASPARAGINE ON THE ENZYMIC HYDROLYSIS  
OF LINTNER SOLUBLE STARCH.

Amino acid.		Cuprous oxide.						
Tyrosine.	Aspara- gine.	Purified pancreatic amylase (No. 60). Mg.	Commercial pancreatin (No. 8). Mg.	Saliva. Mg.	Purified malt amylase (No. 155). Mg.	Malt extract. Mg.	Aspergillus amylase (No. 23). Mg.	Commercial takadiastase (No. 7). Mg.
None	None	282	294	323	248	252	261	287
50	None	318	317	353	262	266	273	299
None	50	316	312	352	256	255	263	291
25	25	317	317	355	263	259	269	296
50	50	322	319	362	263	263	270	297
100	None	—	—	356	—	—	—	—
None	100	—	—	364	—	—	—	—
Activation due to tyrosine		36	23	30	14	14	12	12

TABLE IV.  
EFFECT OF PHENYLALANINE AND PHENYLALANINE PLUS ASPARAGINE ON THE EN-  
ZYMIC HYDROLYSIS OF LINTNER SOLUBLE STARCH.

Amino acid.		Cuprous oxide.						
Phenylal- anine. Mg.	Aspara- gine. Mg.	Purified pancreatin amylase (No. 58). Mg.	Commercial pancreatin (No. 8). Mg.	Saliva. Mg.	Purified malt amylase (No. 155). Mg.	Malt extract. Mg.	Aspergillus amylase (No. 23). Mg.	Commercial takadiastase (No. 7). Mg.
None	None	267	293	207	244	250	252	288
50	None	300	306	222	251	253	261	290
100	None	303	307	225	256	256	263	293
None	50	309	312	225	253	254	259	291
50	50	309	312	225	257	257	264	293
25	25	308	311	225	260	255	261	292
Activation due to phenylalanine		36	14	18	12	6	11	5

The data given in the above tables show an undoubted increase in the activity of purified pancreatic amylase, pancreatin, saliva, and purified malt amylase in the presence of any one of the 4 amino acids investigated or of any 2 of them whose joint effects were tested. The apparent activation is not so marked in case of the less sensitive enzymes, malt extract, takadiastase and aspergillus amylase. It is also true that the acceleration of hydrolysis by the amino acids is somewhat greater for the purified form of the enzyme than for the natural or commercial material in which the enzyme is accompanied by other constituents of the tissue or secretion in question. It will be observed that, in general, the 4 amino acids here discussed as well as asparagine and aspartic acid previously studied<sup>1</sup> behave in a similar manner. The above results show no evidence that the addition of two amino acids to the same digestion mixture causes greater activation than would result from a corresponding concentration of one of them. The following combinations have been tested: aspartic acid and aspar-



agine, glycine and aspartic acid, tyrosine and asparagine, phenylalanine and asparagine, alanine and glycine.

Since some investigators have held that the activating effect of amino acids is attributable to their presence inducing a more favorable hydrogen-ion concentration in the digestion mixture, we have determined electrometrically the hydrogen-ion concentrations of our mixtures with and without neutralized amino acid, with the results shown in Table V. It is evident that the reaction of our mixtures is not changed by the addition of the neutralized amino acids to any significant degree and therefore that the favorable effect of the amino acid upon the enzyme action is due to some other cause or causes.

TABLE V.

MEASUREMENTS OF HYDROGEN-ION CONCENTRATION IN SOLUTIONS WITH AND WITHOUT NEUTRALIZED AMINO ACIDS.

50 mg. of amino acid used in the last four experiments.

Amino acid.	Solution activated as for pancreatic amylase $C_H^+ \times 10^7$ .	Solution activated as for malt amylase $C_H^+ \times 10^8$ .	Solution activated as for aspergillus amylase $C_H^+ \times 10^8$ .
None.....	1.2	3.4	1.2
Glycine.....	1.3	3.1	1.0
Alanine.....	1.3	3.5	1.2
Tyrosine.....	1.3	3.4	1.2
Phenylalanine.....	1.3	3.3	1.2

#### Mode of Action of the Amino Acid.

Several possible explanations of the favorable influence of the amino acids may be suggested.

(1) **Is the Action Direct?**—It is conceivable that the amino acid may directly facilitate the interaction of the enzyme with the substrate. Until our knowledge of the mechanism of enzyme action is further developed this suggestion, while the most direct, can only be approached by somewhat speculative discussion or, experimentally, by a process of elimination of other possibilities.

(2) **Does the Effect Depend upon Some Reaction with the Products of Digestion?**—Since the activity of an enzyme is often diminished by the accumulation of the products of its action, it might be suggested that the amino acids exert their favorable effect through combining with some product or products of the hydrolysis which might otherwise combine with the enzyme itself, thus reducing its activity, or might, if remaining free in the solution, tend to bring the hydrolysis to equilibrium. To test this point, the effect of the addition of 100 mg. of pure maltose to the starch paste, with and without glycine, on hydrolysis by pancreatic amylase was determined. Similar experiments in which a certain amount of a hydrolytic mixture was substituted for pure maltose were carried out as follows. One g. of starch was digested for 1 hour at 40° by pancreatic

amylase, at the end of which time the enzyme was destroyed by boiling. The effect of 25 and 50 cc. of this digested mixture on hydrolysis with and without glycine was tested. Correction being made for the reducing power of maltose or digestion products added, and the amounts of activating salts being properly adjusted, both pure maltose and the hydrolytic products of the starch were found under the conditions of these experiments to be without measurable effect upon the activity of the enzyme used, showing that the favorable influence of amino acids cannot be explained in this way.

(3) **Does the Amino Acid Protect the Enzyme against Some Accidental or Unknown Deleterious Influence?**—Aside from the possibility of correcting an unfavorable hydrogen-ion concentration which has already been excluded as an explanation of our results, it is possible that the amino acid may act by protecting the enzyme from some active but unknown deleterious influence. This is illustrated by the following experiments with cupric sulfate.

*Protective Action of Amino Acids Against Cupric Sulfate.*—These experiments were designed to show whether the deleterious effect upon amylase activity of such a heavy metal salt as copper sulfate could be wholly or in part overcome by the presence of an amino acid. In the experiments the results of which are given in Table VI, the cupric sulfate and amino acid were added to the cooled starch paste and thoroughly mixed before pouring onto the enzyme solution.

TABLE VI.  
ACTION OF AMINO ACIDS IN PROTECTING PURIFIED PANCREATIC AMYLASE  
FROM THE DELETERIOUS EFFECT OF COPPER.

Amino acid.	Mg.	Conc. $\text{CuSO}_4$ in starch paste. <i>M</i> .	Cuprous oxide. Mg.
None.....		None	274
None.....			58
Alanine.....	10		298
Asparagine.....	100	0.00003	293
Glycine.....	100		304
Glycine.....	50		295
Glycine.....	100	None	308

The above data show that a 0.00003 *M* concentration of cupric sulfate in the digestion mixture diminished the activity of pancreatic amylase by about 78%. This is in accordance with results recently obtained in this laboratory and reported in the preceding paper by Sherman and Wayman. However, upon the addition of 0.1% of amino acid, not only is the inhibiting influence of the cupric sulfate counteracted, but there is an increase in saccharification almost equal to that which occurs in the presence of amino acid and absence of copper. Further experiments were performed in which the cupric sulfate was added directly to the enzyme

solution in two concentrations, 0.0035 *M* and 0.00003 *M* and the efficiency of 0.1% glycine in the substrate in reactivating the enzyme was studied. Some results are given in Table VII.

TABLE VII.

REACTIVATION OF PANCREATIC AMYLASE BY GLYCINE AFTER INACTIVATION BY COPPER.

Glycine. Mg.	Conc. CuSO <sub>4</sub> in starch paste. <i>M</i> .	Conc. CuSO <sub>4</sub> in enzyme solution. <i>M</i> .	Conc. CuSO <sub>4</sub> in digestion mixture. <i>M</i> .	Cuprous oxide.		
				Expt. 1. Mg.	Expt. 2. Mg.	Expt. 3. Mg.
None	100	None	None	280	252	264
100		None	None	316	—	300
None		0.0035	0.00003	98	—	—
None	0.00003	0.00003	$1.8 \times 10^{-7}$	—	209	—
		0.00003	$1.8 \times 10^{-7}$	—	260	184
		0.00003	0.00003	—	260	182

Numerous experiments showed that the inactivation of the enzyme by the copper and its reactivation by amino acid were considerably influenced by time and temperature. In Expt. 2 of Table VII the solution stood for about 12 minutes before testing; in Expt. 3 it stood for 55 minutes. The influence of temperature is illustrated in Table VIII.

TABLE VIII.

EFFECT OF TEMPERATURE ON REACTIVATION OF PANCREATIC AMYLASE BY GLYCINE.  
After standing for 20 min. in cupric sulfate solution 0.00003 *M*.

Glycine. Mg.	Temp. of enzyme sol. after 20 min. °C.	Cuprous oxide. Mg.
None	23	115
100	23	142
None	12	175
100	12	213

As to the bearing of these experiments with cupric sulfate upon the question whether the role of amino acids is that of a direct accelerator of the enzyme action or rather that of a protector which increases the amount of work done by the enzyme through preventing its deterioration, it cannot be doubted that they establish the possibility of a very marked protective effect without precluding the additional possibility of a more direct action upon the enzyme.

Evidently with a low concentration of copper ions in solution these react with amino acid forming copper-amino ions<sup>4</sup> more readily than with the enzyme; and moreover, when the copper ion has already acted upon and inactivated a part of the enzyme, it apparently may still be taken up by the amino acid, and the enzyme thus freed from the copper may become active again.

(4) Does the Amino Acid Act by Retarding the Hydrolytic Destruction of the Enzyme?—Another possibility is that the amino acid may act

<sup>4</sup> See J. T. Barker, *Trans. Faraday Soc.*, 3, 188 (1908).

by preventing or retarding the deterioration of the enzyme in its aqueous solution. The very rapid deterioration of water solutions of pancreatic amylase, particularly when highly purified, and the influence of the sodium chloride and secondary phosphate (regularly used to "activate" this enzyme) in retarding the deterioration have been discussed in previous papers from this laboratory.<sup>5</sup> Since the deterioration of enzymic activity, while greatly retarded, is not entirely prevented by the presence of the salts, it is not improbable that the favorable influence of the amino acid may be due at least in part to a further protection of the enzyme from deterioration in the aqueous dispersion in which it acts.

This we have found to be the case, solutions of pancreatic amylase which had stood for 1 hour at 40° showing about 1/3 greater amylase activity when alanine had been added to the solution in advance. The conditions in this case were such as to result in greater deterioration than occurs in our ordinary tests of enzyme activity, both because of longer exposure of the enzyme to warm water and because it remained longer in water in the absence of its substrate. A series of similar experiments at different temperatures is now in progress, and the results thus far obtained go to show that the influence of the amino acid becomes more marked at the higher temperatures at which the enzyme is undergoing more rapid deterioration, thus strengthening the impression that the amino acid tends to preserve the enzyme from the destructive action of the water. Further discussion is best deferred until the completion of the projected series of experiments. Meantime, the now fully demonstrated fact that the presence of certain amino acids retards the deterioration of the enzyme constitutes an interesting addition to the evidence supporting the view that the enzyme itself is a substance of protein nature or which contains protein as an essential constituent.

### Summary.

Addition of glycine, alanine, phenylalanine or tyrosine caused an undoubted increase in the rate of hydrolysis of starch by purified pancreatic amylase, commercial pancreatin, saliva, or purified malt amylase. Less marked results were obtained with the less sensitive enzyme materials, malt extract, takadiastase, and an aspergillus amylase product prepared in the laboratory from takadiastase.

Each of the 4 amino acids here studied, as well as aspartic acid and asparagine previously investigated, showed a similar favorable influence upon the enzymic hydrolysis of the starch.

The addition of a mixture of two of these amino acids, produced no greater effect than would result from the same concentration of one of them. In these experiments the favorable effect of the added amino acid was

<sup>5</sup> Sherman and Schlesinger, *This Journal*, and in other papers of this series.

not due to any influence upon hydrogen-ion concentration nor to combination of the amino acid with the product of the enzymic reaction.

On the other hand it is shown that the addition of one of these amino acids is a very effective means of protecting the enzyme from the deleterious effect of cupric sulfate and may even serve to restore to full activity an enzyme which has been partially inactivated by copper.

The favorable influence of the amino acid is evidently due in part at least to a protection of the enzyme from deterioration in the aqueous dispersion in which it acts.

The establishment of the importance of the last mentioned factors does not preclude the possibility of a more direct influence of the amino acid upon the activity of the enzyme.

The investigation is being continued by studying the effects of the above amino acids through a wider range of times and temperatures and by extending the study to additional amino acids.

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

NEW YORK CITY.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 376.]

## A STUDY OF THE INFLUENCE OF ARGININE, HISTIDINE, TRYPTOPHANE AND CYSTINE UPON THE HYDROLYSIS OF STARCH BY PURIFIED PANCREATIC AMYLASE.

By H. C. SHERMAN AND MARY L. CALDWELL.

Received July 22, 1921.

Previous work in this laboratory<sup>1</sup> having shown that various mono-amino acids tested exhibit quite uniformly the property of increasing the enzymic hydrolysis of starch, especially by pancreatic amylase, the experiments here described were planned to extend the investigation to amino acids of different types of structure.

Arginine and histidine solutions were prepared from casein and gelatin by Kossel's method<sup>2</sup> with slight modifications developed in the course of this work. In the latter part of the work commercial preparations<sup>3</sup> of histidine dichloride and tryptophane were also used. The cystine used was prepared by another worker in this laboratory.<sup>4</sup> In certain of the experiments we have also made use of glycine obtained commercially<sup>5</sup> and an imported phenylalanine.

The enzyme used was a pancreatic amylase preparation (No. T-19-B) purified

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<sup>1</sup> Sherman and Walker, *THIS JOURNAL*, **41**, 1866 (1919); and the preceding paper.

<sup>2</sup> Kossel, *Z. physiol. Chem.*, **31**, 165 (1900-1).

<sup>3</sup> Purchased from the Special Chemicals Company.

<sup>4</sup> Alice Thompson Merrill, *Dissertation*, Columbia University, 1921.

<sup>5</sup> From Eimer and Amend.

in this laboratory as previously described.<sup>6</sup> As substrate we used a commercial<sup>7</sup> "Soluble Starch according to Lintner" after purification by washing 9 times with distilled, and 6 times with thrice distilled, water. In weighing out portions of starch for test, allowance was made for its moisture content. Both the soluble starch to be used as substrate, and each amino acid to be tested, was titrated with 0.01 *N* sodium hydroxide solution or hydrochloric acid using rosolic acid as indicator. From the results of these titrations the amounts of 0.01 *N* alkali needed to neutralize the soluble starch, and of acid or alkali needed to neutralize each of the amino acids used, were calculated and these amounts were added to the starch dispersions and the amino acid solutions in preparing them for the experiments to be described. The hydrogen-ion concentrations of the starch pastes with and without the addition of the neutralized amino acid solutions were then verified by electrometric determinations and by the indicator method as explained below.

In the purification of all materials, and the cleaning and protection of all apparatus used in the experiments we have observed the precautions described in previous papers from this laboratory.

### Method.

Preliminary experiments showed that the gravimetric method worked out in this laboratory for determining the saccharogenic power of the enzyme<sup>8</sup> could not be used in the presence of arginine and histidine because of their interference with the determination of reducing sugar by Fehling solution. This had also been found to be true with cystine. For this reason the amylolytic power of the amylase was measured instead.

The procedure followed was based on the method of Wohlgemuth<sup>9</sup> and has been previously used and described in this laboratory.<sup>10</sup> Enough starch to make 600 cc. of a 1% starch paste was weighed out, mixed with 50 cc. of thrice distilled water and poured into 100 cc. of boiling water. The paste was boiled for 3 minutes, cooled, and 25 cc. poured into each of six 100cc. cylinders. To each of these were added the proper activating agents (5 cc. of *M* sodium chloride solution and 2.5 cc. of 0.02 *M* disodium phosphate), enough 0.01 *N* sodium hydroxide solution to neutralize the acidity of the starch, and the amino-acid to be tested, which was also properly neutralized. The mixture in each cylinder was then made up to 100 cc. with thrice distilled water and carefully stirred.

Forty-two clean, dry test-tubes were placed in a special wire frame basket in a bath of ice-water, and carefully measured portions of enzyme solution introduced into each by means of a 1cc. pipet which was accurately standardized and graduated to 0.01 cc. Portions of 5 cc. of one of the starch pastes prepared above were then introduced into each of 7 test-tubes. This was done carefully by means of a buret with a very long delivery tip reaching to the bottom of the test-tube. In this way the lodging of any

<sup>6</sup> THIS JOURNAL, 41, 1855 (1919).

<sup>7</sup> From Merck and Company.

<sup>8</sup> THIS JOURNAL, 32, 1082 (1910); 37, 628 (1915).

<sup>9</sup> Wohlgemuth, *Biochem. Z.*, 9, 1 (1908).

<sup>10</sup> THIS JOURNAL, 37, 634 (1915).

of the starch paste on the sides of the tube was avoided. Since the tubes were kept in ice-water no measurable reaction took place.

The basket of tubes so prepared was shaken and placed in a Freas thermostat in which the temperature varied only about  $\pm 0.01^\circ$ . The tubes were thus kept at an average temperature of  $40^\circ$  for 30 minutes, when the basket was taken out and placed in ice-water to stop the action of the enzyme. After a few minutes' cooling 0.1 cc. of 0.1 *N* iodine in potassium iodide solution was added to each tube. This was done very carefully by means of a dropping bottle which delivered drops of 0.1 cc. About 20 cc. of distilled water was then poured into each tube and the contents thoroughly mixed. Each set of tubes containing the same amount of the same starch paste with various amounts of enzyme was then observed for the end-point; that is, the tube of lowest enzyme concentration which is definitely red and shows no blue or violet color due to starch.<sup>11</sup> To obtain the value of the amylolytic power of the enzyme, the weight of the 1% starch paste, (5000 mg.) is divided by the weight in mg. of enzyme present in the tube showing "the Wohlgemuth end-point" *i. e.*, the first red color not tinged by violet. Blank determinations were always made in each set; that is, starch pastes neutralized and containing the proper activators but not amino acids were used as the standard each time, since results vary slightly from day to day due to deterioration of the enzyme in solution and possibly other factors.

### Data of Typical Experiments.

Table I shows the influence of 50 mg. of arginine and 50 mg. of histidine on the amylolytic action of the amylase. It will be seen that the arginine has a distinct activating influence, while the histidine has not. These results were confirmed by other experiments.

TABLE I.  
INFLUENCE OF ARGININE AND HISTIDINE ON AMYLOCLASTIC ACTION.

Enzyme, mg. Amino acid.	Power.	0.003.	0.004.	0.005.	0.006.	0.007.	0.008.	0.009.
None	625,000	Blue-violet	Violet	Red-violet	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red
Arginine (gelatin-a) 50 mg.	714,000	Violet-blue	Violet	Red-violet	Violet-red	Red <sup>a</sup>	Red-orange	Orange
Arginine (gelatin-b) 50 mg.	714,000	Blue	Violet	Red-violet	Violet-red	Red <sup>a</sup>	Orange-red	Orange
Histidine (casein) 50 mg.	625,000	Violet-blue	Blue-violet	Violet	Red-violet	Violet-red	Red <sup>a</sup>	Orange-red
Histidine (pur-chased) 50 mg.	625,000	Blue	Blue-violet	Red-violet	Violet-red	Violet-red	Red <sup>a</sup>	Red-orange

<sup>a</sup>The "end-point tube."

<sup>11</sup> The terms used in describing the colors are those of the Milton Bradley Standard Color Chart as given by Mullikin in his "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1904.

The results of a comparison of the influence of arginine and glycine on the amylolytic action of the amylase are given in Table II. Here it is seen that both glycine and arginine activate the hydrolysis, that the activation is about the same, that a 50mg. mixture of the two gives about the same results as 50 mg. of either alone, and that a 100mg. mixture of 50 mg. of each does not seem to increase the effect.

TABLE II.  
INFLUENCE OF ARGININE AND GLYCINE ON AMYLOCLASTIC ACTION.

Enzyme, mg. Amino acid.	Power.	0.003.	0.004.	0.005.	0.006.	0.007.	0.008.	0.009.
None	625, 000	Blue	Violet-blue	Violet	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red
Glycine	714, 000	Blue	Blue-violet	Red-violet	Violet-red	Red <sup>a</sup>	Orange-red	Red-orange
50 mg.								
Arginine	714, 000	Violet-blue	Red-violet	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red	Red-orange
50 mg.								
Glycine Arginine	714, 000	Blue-violet	Violet-red	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red	Orange-red
25 mg. each								
Glycine Arginine	714, 000	Blue	Violet	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red	Orange-red
50 mg. each								
None	625, 000	Blue	Blue-violet	Violet	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red

<sup>a</sup> The end-point tube.

A comparison of the influence of glycine, phenylalanine, cystine and tryptophane was made. The results are given in Table III. They show that activation is produced with each of these amino acids except tryptophane. Previous work<sup>12</sup> has shown that glycine and phenylalanine also activate the saccharogenic power of this amylase.

TABLE III.  
INFLUENCE OF GLYCINE, PHENYLALANINE, CYSTINE and TRYPTOPHANE ON AMYLOCLASTIC ACTION.

Enzyme, mg. Amino acid.	Power.	0.004.	0.005.	0.006.	0.0065.	0.007.	0.0075.	0.008.
None	714, 000	Violet	Red-violet	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red	Orange-red
Glycine	833, 000	Violet	Violet-red	Red <sup>a</sup>	Red	Orange-red	Red-orange	Orange
50 mg.								
Phenylalanine	833, 000	Red-violet	Violet-red	Red <sup>a</sup>	Red	Orange-red	Red-orange	Red-orange
50 mg.								
Cystine	833, 000	Violet	Violet-red	Red <sup>a</sup>	Red	Orange-red	Red-orange	Red-orange
50 mg.								
Tryptophane	less than	Blue-violet	Violet	Red-violet	Red-violet	Violet-red	Violet-red	Violet-red
50 mg.	625, 000							
None	714, 000	Violet	Violet-red	Violet-red	Violet-red	Red <sup>a</sup>	Orange-red	Orange-red

<sup>a</sup> The end-point tube.

<sup>12</sup> Sherman and Walker, THIS JOURNAL, 43, 2461 (1921).



Table IV shows that results obtained with histidine and tryptophane are similar when tested side by side; but as suggested by the foregoing experiments the activity of the enzyme was slightly lower in the presence of the tryptophane than of the histidine.

TABLE IV.  
INFLUENCE OF HISTIDINE AND TRYPTOPHANE ON AMYLOCLASTIC ACTION.

Enzyme, mg. Amino acid.	Power.	0.004.	0.005.	0.006.	0.0065.	0.007.	0.0075.	0.008.
None	714,000	Violet	Red- violet	Violet- red	Violet- red	Red <sup>a</sup>	Orange- red	Red- orange
Histidine (casein) 50 mg.	714,000	Blue- violet	Violet- red	Violet- red	Violet- red	Red <sup>a</sup>	Orange- red	Red- orange
Histidine (pur- chased) 50 mg.	714,000	Blue- violet	Violet	Violet- red	Violet- red	Red <sup>a</sup>	Orange- red	Orange- red
Tryptophane 50 mg.	666,000	Violet- blue	Blue- violet	Violet- red	Violet- red	Violet- red	Red <sup>a</sup>	Red
None	714,000	Violet	Violet- red	Violet- red	Violet- red	Red <sup>a</sup>	Orange- red	Orange- red

<sup>a</sup> The end-point tube.

In Table V the results of a further comparison of the influence of the different preparations of histidine are given. As before, no activation is seen. (Duplicate determinations are omitted.)

TABLE V.  
INFLUENCE OF HISTIDINE ON AMYLOCLASTIC ACTION.

Enzyme, mg. Amino acid.	Power.	0.004.	0.005.	0.006.	0.0065.	0.007.	0.0075.	0.008.
None	714,000	Violet	Violet- red	Violet- red	Violet- red	Red <sup>a</sup>	Orange- red	Orange- red
Histidine (casein) 50 mg.	666,000	Violet	Red- violet	Red- violet	Violet- red	Violet- red	Red <sup>a</sup>	Red
Histidine (pur- chased) 50 mg.	714,000	Blue- violet	Red- violet	Violet- red	Violet- red	Red <sup>a</sup>	Red	Orange- red
Histidine (gelatin) 50 mg.	666,000	Violet- blue	Violet	Violet- red	Violet- red	Violet- red	Red <sup>a</sup>	Orange- red
None	714,000	Blue- violet	Red- violet	Violet- red	Violet- red	Red <sup>a</sup>	Orange- red	Red- orange

<sup>a</sup> The end-point tube.

It is interesting to note that the same result was obtained with different samples of histidine prepared from three different sources. (The purchased histidine dichloride was prepared from blood corpuscles by the method of Hanke and Koessler.)<sup>13</sup>

### Discussion.

In order to show whether the results obtained were due to some specific action of the amino acids themselves or to a change in the hydrogen-ion

<sup>13</sup> Hanke and Koessler, *J. Biol. Chem.*, **43**, 521 (1920).

concentration of the hydrolysis mixtures due to the addition of the amino acids, careful measurements were made of the hydrogen-ion concentrations in the starch pastes as prepared for the experiments. The results are given in Table VI and show that a practically uniform hydrogen-ion concentration of about  $10^{-7}$  was maintained in the different hydrolysis mixtures. This concentration had previously been found to give the optimum saccharogenic activity<sup>14</sup> of this amylase. In a few cases, determinations of the hydrogen-ion concentrations were made in the starch pastes both before and after digestion but no difference was found.

TABLE VI.

HYDROGEN-ION CONCENTRATION IN MOLES PER LITER AS FOUND IN THE DIGESTION MIXTURES USED.

50 mg. of amino acid used in each case.

Starch paste plus.	$C_H^+$ (electrometric) $\times 10.7$	$C_H^+$ (colorimetric) $\times 10.7$
No amino acid.....	1.1	1.1
Arginine, (gelatin-a).....	1.2	1.1
Arginine, (gelatin-b).....	....	1.1
Glycine.....	1.1	1.1
Histidine, (casein).....	1.0	1.6 to 1.1
Histidine, (gelatin).....	...	1.1
Histidine, (purchased).....	1.1	1.6 to 1.1
Tryptophane.....	1.1	1.1
Cystine.....	...	1.6 to 1.1
Phenylalanine.....	...	1.1

The colorimetric determinations of the hydrogen-ion concentrations were made with Sorensen's phosphate buffer mixtures, as described by Clark,<sup>15</sup> as standards. The electrometric determinations were made with the Clark<sup>16</sup> rocking electrode.

Since sodium chloride and disodium phosphate were present in optimum concentration in all cases, the effects of the added amino acids cannot be due to mere change in the concentration of electrolytes in the hydrolysis mixtures.

The possible influence of a reaction between iodine and tryptophane or histidine was considered and by experiments with different measured amounts of the iodine test solution, controlled by suitable blank tests, it was shown that this was not the reason for the difference in behavior of the tryptophane and histidine compared with the other amino acids.

It is plain from the evidence presented in this and previous papers that most amino acids such as result from hydrolysis of common proteins have

<sup>14</sup> THIS JOURNAL, 41, 231-235 (1919).

<sup>15</sup> "Determination of Hydrogen Ions," by W. M. Clark, Williams and Wilkins, 1920, p. 76.

<sup>16</sup> Clark, *J. Biol. Chem.*, 23, 475-86 (1915).

a favorable influence upon the hydrolysis of starch by pancreatic amylase, while tryptophane and histidine do not.

The favorable influence shown by arginine, cystine, and all of the mono-amino acids which have been tested, may be attributed either to a direct or an indirect effect, or to both.

Let us consider first the hypothesis of direct action. Since all the amino acids here considered contain the  $\alpha$ -amino group to which it would seem that any direct activating influence must be attributed (since this is the feature which they possess in common, and the only feature to which the activating influence of glycine can be ascribed) it would follow that the negative results obtained with histidine and tryptophane must be due to some inhibitory influence exerted by their respective heterocycles.

We may, however, also conceive the favorable influence of the amino acids as being exerted not directly upon the interaction of the enzyme and the starch but rather through protecting the enzyme from deterioration in the aqueous dispersion in which it acts. In previous papers from this laboratory many observations have been recorded which seem to find their best explanation in the view that the enzyme is itself a substance of protein nature or containing protein as an essential constituent. The deterioration of the enzyme in water is markedly accelerated by rise in temperature and at the heat at which the enzyme activity is rapidly and permanently lost there is evidence of the splitting of protein substance into an albumin which coagulates and a non-coagulable product or products of hydrolysis. This and observations upon loss of enzyme activity during dialysis support the view that the deterioration of the enzyme in water is due to the hydrolysis by the water of the protein material which makes up the enzyme molecule or an essential part of it. Such hydrolysis should be retarded, and the activity of the enzyme therefore conserved, by the presence of any of the amino acids which would be formed as hydrolytic products. This would account for the fact that so many amino acids have such similar effects, since they are all products of the hydrolysis of protein material of which our purified enzyme preparations are essentially composed. The extreme sensitiveness and instability of purified pancreatic amylase in water suggests that the loss of activity probably coincides with a relatively early stage of its hydrolysis. Hence if we conceive tryptophane and histidine to be so bound in the enzyme molecule that their liberation would occur only at late stages of hydrolysis when the enzyme activity had already been lost, we should have an explanation of the difference in behavior between these and other amino acids entirely consistent with the view that the favorable influence of amino acids generally is exerted through conservation of the enzyme rather than through direct activation of it, and need not necessarily be influenced by the differences of structure which exist among the amino acids themselves.

In other words according to one hypothesis the explanation of the differences observed in our experiments with different amino acids would be sought in the structure of the amino acid radical, and according to the other, in the structure of the enzyme molecule. In our opinion both of these hypotheses may be correct and experiments designed to throw further light upon them are now in progress.

### Summary.

Two preparations of arginine obtained from gelatin, and two of histidine, one from gelatin and the other from casein, were tested for their influence upon the action of the enzyme in comparison with blank tests, with the mono-amino acids, glycine and phenylalanine, with each other, with purchased preparations of histidine and tryptophane, and with cystine prepared by another worker in this laboratory.

Tested by measuring the amylolytic action of purified pancreatic amylase upon "soluble" starch, it has been shown that arginine and cystine, like glycine and phenylalanine, influence favorably the digestion of the starch and that histidine and tryptophane do not. Consistent results were obtained with the two preparations of arginine and the three of histidine.

The tests with all these amino acids were controlled as to hydrogen-ion concentration, in most cases by both the colorimetric and the electrometric methods. It is therefore established that the influence of the amino acid upon the extent of the hydrolysis of the starch by the enzyme is not simply a matter of buffer effect or other effect upon the hydrogen-ion concentration of the digestion mixtures.

Thus it has been shown that the amino acids here studied differ among themselves in their effects upon the enzymic hydrolysis of starch, whereas the different mono-amino acids studied have shown a practically uniform behavior in this respect. Hence it appears that there are specific effects, probably though not necessarily connected with differences of structure, which may offset the favorable influence uniformly shown by the mono-amino acids studied previously. Further experiments are in progress which it is hoped will throw additional light upon the mode of action of the amino acids.

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

NEW YORK CITY.

## NEW BOOKS.

**Physikalisch-chemische Uebungen.** Third enlarged and improved edition. By W. A. ROTH, o. Professor at the Technischen Hochschule in Braunschweig. Leopold Voss, Leipzig, 1921. viii + 278 pp. 75 fig. 23 × 15 cm. Price M 30.

This third edition, according to the preface, is photographically reproduced from the second, with 30 pages of additions necessitated by the progress of the science meanwhile. Chief among these is a 20-page section on colloid chemistry, based largely upon an introductory course formerly given by Freundlich at Braunschweig.

In the reviewer's opinion neither the changes from the first edition, nor the 10 pages of additions not concerned with colloid chemistry, suffice to bring the book up to date. At least the author should have included references to the most fundamental contributions to physico-chemical method in the last 10 years.

Waiving the 10-year limit, the reader finds only the Ostwald gas regulator for thermostats, with no mention of the possibilities of electrical heating. For the determination of the density of solids, the ancient specific-gravity bottle, with ground-glass stopper surmounted by a capillary, is still recommended. No mention is made of adiabatic calorimetry, and while there is a reference to Regnault-Pfaundler, the only method for cooling correction described is this: Correct the first half of the readings in the reaction period by the average temperature coefficient in the preliminary period, and the second half of the readings in the reaction period by the average temperature coefficient in the final period.

With the present book as his sole guide, a student could doubtless learn to perform a great variety of measurements with accuracy sufficient for most purposes. But his appreciation of modern possibilities in such work, and his critical powers, dealing with the relative importance of errors, and the underlying principles for their elimination, might be more fully developed.

G. S. FORBES.

**Physical Chemistry for Colleges.** A Course of Instruction Based upon the Fundamental Laws of Chemistry. First Edition. By E. B. MILLARD, Assistant Professor of Physical Chemistry, Massachusetts Institute of Technology. International Chemical Series, H. P. Talbot, Ph. D., Consulting Editor. McGraw-Hill Book Company, Inc., New York, 370 Seventh Avenue; London, 6 and 8 Bouverie Street, E. C. 4. 1921. vii + 411 pp. 61 fig. 14.5 × 21 cm. Price \$3.50.

In this text the author has sought "to bring before college students certain of the more important aspects of physical chemistry, together with accurate modern data which illustrate the applicability of its laws to the phenomena observed in the laboratory." He attempts to emphasize the limitations of the "orthodox laws" of physical chemistry, feeling that "a trusting belief in inadequate physical laws will only retard the scientific progress of the student, and weaken his faith in adequate laws; whereas

a wholesome appreciation that physical chemistry is an unfinished and growing science may stimulate thoughtfulness and research." In his laudable efforts to present a book which is thoroughly up to date the author has paid particular attention to the work of the last decade or so and has omitted much which might better have been included. Tastes differ, but the reviewer has a natural predilection for a certain amount of historical treatment of the subject. The names of van't Hoff, Ostwald, Nernst, Arrhenius, Kohlrausch, Hittorf, Berthelot, Thomsen, Guldberg and Waage, and many others are closely associated with the development of the subject of physical chemistry, in the reviewer's mind at least, yet in this text these investigators and theorists are all but ignored, while there are numerous references to men who have contributed comparatively little to the subject and whose scientific achievements are of comparatively little importance. The development of physical chemistry is one of the most delightful romances in history and the student who is deprived of the personal side of the story not only misses much that is due him but fails to have his enthusiasm and interest aroused. The recital of bare facts shorn of their historical and personal setting is not stimulating.

The reviewer does not believe that students profit greatly by being fed ready-made formulas. Unless they understand the development of the formula its significance is largely lost. All through this book there is a regrettable lack of development and explanation of formulas. For example, the Nernst formula for electromotive force bobs up unannounced.

No development, no explanation, not even the name of Nernst associate with it! The Gibbs-Helmholtz equation fares somewhat better, inasmuch as it is given by name, but it is not developed and the student must take it for granted and swallow it. The frequent repetition of this process must necessarily lead to much mental indigestion.

The book has many excellent qualities and will be of interest to the teacher who desires to brush up on the later developments of his subject and bring his teaching up to date. As a text it is not sufficiently comprehensive and complete for a full year's course such as is now given in most universities, but may serve where a shorter course is given and where the bare facts only are wanted. The author has brought his treatment up to date and has given many excellent examples in his problem work which supplant the time-honored ones. If a student conscientiously solves the problem work laid out he will learn a great amount of solid physical chemistry.

The statements of the fundamental laws and theories are good. A more complete discussion of fundamental units and the methods whereby they are fixed would be welcome, as the average student gets a very hazy idea of this part of the subject. The presentation of the gas laws and equations is good and the development of the kinetic equation and that

of van der Waals is satisfactory. It is believed that a discussion of the commercial liquefaction of gases might well have been included to arouse the interest of the student if for no other reason. The chapter on Solid Substances is modern and well written. Chapter V on Solutions is a mixture of "ideal solutions," "vapor pressure of solutes," "distribution between phases," "vapor pressure of ideal solutions of two liquids," "constant temperature distillation," "boiling point of solutions," "fractional distillation," "mixtures with a minimum boiling point," "distillation with steam," "freezing point of solutions," "molecular weights," and "osmotic pressure." There is no natural sequence in this arrangement nor is there any development of the relations between osmotic pressure on the one hand and boiling-point elevation, lowering of the vapor pressure and freezing-point lowering on the other. The only reference to van't Hoff is an erroneous inference that the term "osmotic pressure" was originated by him in 1886, and Pfeffer's classical work is entirely ignored. By inference (p. 141) again the student is led to believe that osmotic pressure is due to sieve action. In discussing freezing-point lowering the impression is given that thermocouples are necessary for accurate work; and in the discussion of the elevation of the boiling point the only apparatus mentioned is one first described in the literature in 1919. In Chapter VI transference numbers are discussed but no mention is made of Hittorf and his classical researches. Kohlrausch's law is not mentioned as such nor is it stated as a law.

The Chapter on Thermochemistry is excellent though one misses mention of Berthelot and Thomsen. In fact there is but one reference to work done previous to 1910.

Chapters VIII and IX deal with homogeneous and heterogeneous equilibria. In the main the treatment is good and the data well chosen with the possible exception of the example of the equilibrium between sulfur and water. While giving empirical equations for ionization, the Bates equation might well have been mentioned along with that of Kraus and Bray. The author has done well to include a discussion of indicators—a subject usually omitted.

The chapter on Kinetics of Reactions (X) contains a distinct surprise in that the important subject of catalysis is disposed of in half a page. This is indeed a serious omission inasmuch as the subject of catalysis is one of the most important in the whole realm of physical chemistry.

In Chapter XI there is given a very short discussion of the tremendously important subject of Physical Properties and Molecular Structure. This chapter should be considerably expanded and an adequate presentation made of molecular refraction and optical activity. Most of us prefer the equation of Lorentz and Lorenz for molecular refraction rather than the empirical equation of Gladstone and Dale which the author has given, and

the reviewer cannot subscribe to the inference (p. 313) that optical activity is not properly the concern of the physical chemist.

In Chapter XII we have a brief presentation of the periodic table from the modern view point, a presentation which serves well as an introduction to the two succeeding chapters. Chapter XIII gives us an excellent elementary presentation of the fundamental facts relating to Radiochemistry. This chapter and the one following (Atomic Structure) are the most interesting ones in the book and are the ones which will be of most inspirational value to the student. They are particularly acceptable because they present in an interesting way the fundamental facts and modern theories which are being much discussed at the present time. These two chapters are distinctly the high spots in the whole book.

The subject of Colloids (Chap. XV) occupies but 13 pages and suffers from the compression. The importance of Colloid Chemistry in the industries and in daily life is nowhere emphasized and there is little in the chapter to arouse the interest of the student. The final chapter is devoted to electrochemistry.

The appearance of the text is good. There are comparatively few typographical errors and most of them are obvious. The binding of the copy sent to the reviewer was not good.

In a book review the good qualities are too easily submerged. The book in question contains much that is interesting and valuable and the treatment is not a rehash of books that have gone before.

J. H. MATHEWS.

**Some Microchemical Tests for Alkaloids.** BY CHARLES H. STEPHENSON, Scientific Assistant, Bureau of Chemistry, U. S. Department of Agriculture. **Chemical Tests of the Alkaloids Used.** BY C. E. PARKER, Assistant Chemist, Bureau of Chemistry, U. S. Department of Agriculture. J. B. Lippincott Company, East Washington Square, Philadelphia, Pa., 1921. 110 pp. XXVII Plates (162 photographs). 15.5 X 23.5 cm.

The first compilation of data in a comparatively new field is always an arduous and usually a thankless task: welcomed it is true by fellow workers in the field but rarely appreciated at its full worth. Most of us wonder why the author could not have included more constants, could not have been more specific in his descriptions and included more chemistry in his discussions. Most chemists into whose hands this little book will come will doubtless ask these questions and will be inclined to lay aside the book with a feeling of disappointment. It is only after a careful examination that the reader will appreciate the time and the labor which have been expended in its preparation. It is to be regretted, however, that with so excellent a beginning the work was not completed and that the authors did not give us a comprehensive handbook on the chemical microscopy of the alkaloids, a book which is sorely needed.



The behaviors of 64 alkaloids in varying concentrations with a large number of reagents have been studied under the microscope, and the results which were obtained are briefly described by the author. These descriptions are, in the main, confined to statements of whether crystalline or amorphous precipitates were obtained; in a few instances the reader is told that the crystals formed in the reaction polarize, but in no case is the reader informed as to the character of the extinction, the crystal system or other optical properties of the crystals which are formed, data invaluable in the identification of compounds under the microscope. It is the absence of these data that detracts much from the value of the book for the chemist and the toxicologist. The data presented appear to have been compiled solely from the view point of, and for the average microscopist who is interested only in whether a given reagent will or will not cause the separation of crystals when added to a drop of an alkaloidal solution. Nowhere does the author introduce any statements concerning the chemistry of the alkaloids or of the reactions obtained, nor has he taken advantage of our knowledge of the constitution of many of the common alkaloids and employed organic compounds as reagents and thus obtained identity tests based upon chemical constitution. It is largely due to this lack of chemistry in our literature relating to chemical microscopic tests that the development of chemical microscopy has been retarded and that chemists do not take more kindly to this type of qualitative analysis. The method adopted by the author for performing the tests, "Place one drop of the alkaloidal solution on a microscope slide and add, by means of a glass rod, one small drop of the reagent," is not always conducive to the best results nor can we thus obtain the most uniform and most characteristic crystals.

The photomicrographs illustrating the crystal forms which were obtained in the different tests are excellent and exceptionally well executed. They represent a high degree of skill and have been selected with care and good judgment. An index to the plates adds greatly to their usefulness for ready reference.

Had the arrangement adopted in the first 83 pages (large type headings) been retained in the pages devoted to, "Chemical Examinations" (pp. 84-105) or if an index to the text had been added, it would have materially improved the book and saved the reader time and annoyance. As it is, the discussion of one alkaloid follows immediately after another without change of type or spacing, so that the chemical tests upon a given alkaloid are not quickly found.

As a guide for the beginner in the microscopic detection of the alkaloids, this book, aside from its excellent photographs, has little to recommend it; but considered as a compilation of facts relative to the behavior of alkaloidal solutions toward a number of inorganic reagents it is a distinctly valuable contribution to our heretofore meagre knowledge of these tests and should

find a place upon the shelves of all analysts who have occasion to make analyses of alkaloid-containing materials.

E. M. CHAMOT.

**The Physiology of Protein Metabolism.** Second Edition. By E. P. CATHCART, M. D., D. Sc., F. R. S., Gardiner Professor of Chemical Physiology, University of Glasgow. Longmans, Green and Co., Fourth Ave. and 30th Street, New York; 39 Paternoster Row, London; Bombay, Calcutta and Madras; 1921, viii + 178 pp. 15.5 X 24.5 cm. Price \$4.25 net.

The second edition of this very important and well balanced volume covers essentially the same field as that of the first edition. Since the appearance of the first edition in 1912 many epoch making investigations have been recorded and in the present edition a successful attempt has been made to bring the book up to date. To this end many sections have been entirely rewritten and a new chapter has been added summarizing the influence of the non-nitrogenous foodstuffs on the metabolism of protein. For the student of nutrition the book is invaluable.

FRANK P. UNDERHILL.

**Die Schwimmaufbereitung der Erze.** By PAUL VAGELER. Theodor Steinkopff, Dresden and Leipzig, 1921. pp. v + 98. 23 X 16 cm. Price 4 shillings, 4 pence.

The author was apparently captured in German Southwest Africa during the war and he learned about ore flotation from the English. On p. 6 he points out how much better the Germans study such matters than the Anglo-Saxons. The reviewer does not feel called upon to praise the scientific studies of Minerals Separation; but the author has not carried the matter very far. He states that adsorption is a factor—which everybody knows—and there he stops. There is no adequate discussion of froth formation; there is nothing serious in regard to the difference, if any, between insoluble and soluble flotation agents; there is nothing to show where the ore particles are in the froth though that was a matter of some apparent importance in one of the trials; there is nothing to show why saponin acts as it does; and the Tennessee experiment of adding copper sulfate to a zinc ore is mentioned as an unexplained mystery. There is no question but that several Anglo-Saxons could have written a much better book than this. It is in the general style of Wolfgang Ostwald—high-sounding phrases and nothing that one can take hold of as definite.

There is also a good deal of padding in the book. The diagrammatic pictures of the neutral helium atom and of the oxygen molecule have very little to do with the problems of ore flotation. On the other hand, it is true, though rather obvious, to say, p. 85, that the advantages of the flotation method are relatively less the greater the cost of grinding. The book is utterly inadequate and it is difficult to see how it can be helpful to anybody.

WILDER D. BANCROFT.

THE JOURNAL  
OF THE  
American Chemical Society  
with which has been incorporated the  
American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE UNIVERSITY OF IOWA.]

**THE FREE ENERGY OF DILUTION AND THE ACTIVITIES OF THE  
IONS OF POTASSIUM BROMIDE IN AQUEOUS SOLUTIONS.**

By J. N. PEARCE AND HARRY B. HART.

Received August 2, 1921.

In a study of "The Activity of the Ions and the Degree of Dissociation of Strong Electrolytes," Lewis<sup>1</sup> has calculated the degrees of dissociation of a large number of uni-univalent salts. These calculations are based on the assumption that in solutions of different electrolytes containing a common ion this ion has the same mobility at any one concentration. From the results obtained he finds that in a 0.1 *M* solution the chlorides, bromides and iodides of hydrogen and the alkali metals are all dissociated to practically the same extent. In order to interpret the changes in the transport numbers of the ions which accompany change in concentration he advances two hypotheses: "(1) that all the ions increase in mobility with increasing ion concentration, the increase being relatively greater, the greater the original mobility; (2) that all the ions decrease in mobility with increasing ion concentration, the decrease being greater the smaller the original mobility." He concludes that the first of these hypotheses is the more probable and advances two probable causes for an increase in ionic mobility with increasing concentration. These are: (1) a gradual

<sup>1</sup> Lewis, *THIS JOURNAL*, 34, 1631 (1921).

dehydration, which although undoubtedly present does not play a dominant part, and (2) an added increase in the ordinary conductivity of the electrolyte due to a conduction of the Grotthus type. The additional conduction due to this effect would account for the assumed increase in mobility.

Making the same assumption regarding the independent mobility of the ions, MacInnes<sup>2</sup> also finds that the alkali chlorides are dissociated to the same extent in 0.01 *M* concentration. This observation led him to advance the hypothesis that for the same molal concentration the activity of the chloride ion is a constant and is independent of the cation associated with it. Further on the basis of the striking similarity of the weight and the mobility of the potassium and chloride ions he assumes that these ions have the same activity in a solution of the salt. Using the available electromotive-force data, MacInnes has calculated the activities of the ions in various solutions of potassium chloride and hydrochloric acid.

Noyes and MacInnes<sup>3</sup> have calculated for a wide range of concentrations the mean activity coefficients of the ions of potassium chloride, hydrogen chloride, lithium chloride and potassium hydroxide.

During recent years there has developed the hypothesis of complete dissociation of strong uni-univalent electrolytes. The possibility of complete dissociation was first suggested by Noyes,<sup>4</sup> and the hypothesis has been further substantiated by the work of Milner,<sup>5</sup> Ghosh,<sup>6</sup> Bjerrum,<sup>7</sup> Brönsted,<sup>8</sup> Hill<sup>9</sup> and others. While this hypothesis demands that the electrolyte be completely dissociated at all concentrations, the number of ions actually free at any one time is limited by various factors involved in the solution process. For any given concentration of the electrolyte a definite fraction of the ions are loosely united, as a result of electrostatic attraction, to such an extent that they are not capable of independent activity and mobility. These "bound" ions, therefore, possess the properties which we have usually attributed to undissociated molecules. Hence, there should exist in a solution of an electrolyte an equilibrium between the electrically bound ions and the simple ions which in the "free" state are capable of independent activity and mobility.

In a recent paper Harned<sup>10</sup> has found that the hypothesis of complete

<sup>2</sup> MacInnes, *THIS JOURNAL*, **41**, 1086 (1919).

<sup>3</sup> Noyes and MacInnes, *ibid.*, **42**, 239 (1920).

<sup>4</sup> Noyes, *Int. Congress Arts Sci.*, St. Louis, **4**, 319 (1904).

<sup>5</sup> Milner, *Phil. Mag.*, [6] **23**, 551 (1912); **25**, 753 (1913); **35**, 352 (1918).

<sup>6</sup> Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707 (1918).

<sup>7</sup> Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918); *Z. anorg. Chem.*, **109**, 275 (1920).

<sup>8</sup> Brönsted, *THIS JOURNAL*, **42**, 761 (1920).

<sup>9</sup> Hill, *ibid.*, **43**, 254 (1921).

<sup>10</sup> Harned, *ibid.*, **42**, 1808 (1920).

dissociation is a good working hypothesis. He has also confirmed the MacInnes hypothesis of the independent activity of the ions. Furthermore, he has computed the individual activity coefficients of the hydrogen, sodium, potassium, lithium and chloride ions in concentrations 0.1 to 3.0 *M*.

Up to this time practically all of the work dealing with ionic activities has been confined to a study of the ions in aqueous solutions of the alkali chlorides and hydrochloric acid. We have thought it worth while, therefore, to extend these investigations by a study of the activity of the ions in solutions of potassium bromide, thus making possible a direct comparison of the activities of the chloride and bromide ions.

#### Materials and Apparatus.

Potassium bromide of a high grade was further purified by crystallizing twice from distilled water and twice from "conductivity" water. The mercury used in preparing the amalgam was first repeatedly sprayed through a long column of dil. nitric acid and then distilled in a current of air under reduced pressure.

In preparing the silver bromide electrodes small pieces of platinum foil, in the form of electrodes, were first electrolytically plated with a firm white deposit of metallic silver. They were then arranged as anodes in a solution of potassium bromide and coated with silver bromide, using a current density of 2 m. a. for 15 minutes. The electrodes thus prepared are of a steel-gray color and are easily reproducible to within 0.05 m.v. The potassium amalgam was made by distilling mercury over into metallic potassium, *in vacuo*, after the method of Lewis and Kraus.<sup>11</sup> It was then filtered through a fine capillary into a suitable storage flask and preserved under an atmosphere of pure dry hydrogen. The amalgam used throughout contained 0.2122% of metallic potassium.

Owing to the fact that the oxidation of the potassium by dissolved oxygen materially changes the potential of the amalgam electrodes, every possible precaution was taken to exclude air from the solutions. To this end the exact amount of salt for a given volume concentration was transferred to a volumetric flask fitted with a stopper and a filling device permitting easy transfer of the solution to and from the flask. Water was then added and the solution boiled. To insure the removal of every trace of air a stream of pure hydrogen was bubbled through the boiling solution. The solution was then cooled to the desired temperature and diluted to the desired volume by adding conductivity water which had been similarly treated. The solution was then weighed on a sensitive balance and its molal concentration calculated. At no time thereafter nor during the potential measurements which followed did the solution come into contact with the air.

A large oil-bath electrically controlled gave temperatures constant to 0.02° for any desired temperature. All potential measurements were made on a Wolff potentiometer, using as a standard of reference a recently certified Weston cadmium cell, (No. 3554: 1.01956 volt).

#### Precision and Duplication.

Three silver bromide electrodes having a maximum variation of not more than 0.05 m.v. were placed in each half-cell and allowed to stand until equilibrium was established between the electrodes and the potassium bromide solution. A period of 4 hours was found to be sufficient for this purpose. Only those electrodes in any half-cell were

<sup>11</sup> Lewis and Kraus, *THIS JOURNAL*, 32, 1459 (1910).

used in the measurements which checked, over all, to 0.03 m.v. In case no such agreement was attained the cell was dismantled and set up anew. When at any temperature the electromotive forces had become constant final readings were taken and the temperature changed. In this way the electromotive forces of the various cells were obtained at 25°, 30° and 35°.

### Experimental.

In the present work the following types of cells have been studied: (A)  $\text{Ag} | \text{AgBr, KBr } (c) | \text{K.Hg}_x$ ; (B)  $\text{Ag} | \text{AgBr, KBr } (c_1) | \text{K.Hg}_x - \text{Kg}_x \cdot \text{K} | \text{KBr } (c_2), \text{AgBr} | \text{Ag}$ ; (C)  $\text{Hg}_x \cdot \text{K} | \text{KBr } (c_1), \text{AgBr} | \text{Ag} - \text{Ag} | \text{AgBr, KBr } (c_2) | \text{K.Hg}_x$ ; (D)  $\text{Ag} | \text{AgBr, KBr } (c_1) | \text{KBr } (c_2), \text{AgBr} | \text{Ag}$ ; (E)  $\text{Hg}_x \cdot \text{K} | \text{KBr } (c_1) | \text{KBr } (c_2) | \text{K.Hg}_x$ .

**Measurements of the Cells.**—The amalgam electrodes employed are similar to those first used by Lewis and Kraus,<sup>11</sup> and later by Allmand and Polack.<sup>12</sup> The mean value of the electromotive forces for at least two successive set-ups of this type of cell for any one concentration are given in Table I. The values of the electromotive forces for these different set-ups do not differ by more than 0.10 m.v., except for the 2.8032 *M* concentration where a difference of 0.20 m.v. was observed. The values of the electromotive forces of a cell containing exactly 0.10 *M* concentration of potassium bromide at the three temperatures was calculated by means of an empirical quadratic equation expressing the electromotive force as a function of the concentration. These values are inserted at the bottom of Table I. The electromotive forces for the 0.25258 *M*, 0.10048 *M* and 0.050148 *M* were used in these calculations.

TABLE I.  
ELECTROMOTIVE FORCES OF THE CELLS.  
(A).  $\text{Ag} | \text{AgBr, KBr } (c) | \text{K.Hg}_x$ .

Moles per 1000 cc.	Moles per 1000 g. H <sub>2</sub> O.	<i>E</i> <sub>25</sub> volts.	<i>E</i> <sub>30</sub> volts.	<i>E</i> <sub>35</sub> volts.
2.5000	2.8032	2.0235	2.0089	1.9948
1.0000	1.03486	2.0792	2.0657	2.0518
0.5000	0.51048	2.1108	2.0976	2.0849
0.2500	0.25258	2.1432	2.1308	2.1179
0.1000	0.10048	2.1858	2.1740	2.1624
0.0500	0.050184	2.2183	2.2071	2.1958
0.0100	0.010021	2.2948	2.2848	2.2753
0.0050	0.0050096	2.3289	2.2196	2.3098
0.0010	0.0010017	2.4081	2.4002	2.3927
	0.1000	2.1861	2.1743	2.1627

**The Free-energy Decrease and the Heat-content Decrease Attending the Cell Reaction.**—The free-energy decrease ( $-\Delta F$ ), expressed in joules, attending the reaction in any cell is obtained by multiplying the electro-

<sup>12</sup> Allmand and Polack, *J. Chem. Soc.*, 115, 1020 (1919).

motive force of the cell by 96494. If now we express the free energy decrease as a function of the temperature by means of the equation,

$$(-\Delta F)_t = (-\Delta F)_{25} [1 + \alpha(t-25) + \beta(t-25)^2],$$

we can calculate the temperature coefficients of free energy decrease. These values together with the free energy decrease are collected in Table II. The values for the decrease in heat content  $(-\Delta H)$  attending the cell reaction given in the same table have been calculated with the aid of the thermodynamically derived relation,

$$(-\Delta H)_{25} = (-\Delta F)_{25} [1 - \alpha \times 298.09].$$

TABLE II.

THE FREE-ENERGY DECREASE AND THE HEAT-CONTENT DECREASE ACCOMPANYING THE CELL REACTION.

c.	$(-\Delta F)_{25}$ joules.	$(-\Delta F)_{15}$ joules.	$(-\Delta F)_{35}$ joules.	$\alpha \times 10^4$ .	$\beta \times 10^4$ .	$(-\Delta H)_{25}$ joules.
2.8032	195256	193846	192447	-1448.0	+1.0	279527
1.03486	200630	199328	197985	-1279.0	+3.8	277130
0.51048	203679	202396	201180	-1274.0	+4.7	281036
0.25258	206825	205609	204365	-1133.4	-4.7	276711
0.10048	210916	209778	208659	-1087.5	+1.7	279296
0.050184	214072	212971	211827	-995.7	-2.8	277609
0.010021	221463	220469	219552	-893.0	+4.3	280416
0.005009	224753	223822	222881	-776.0	-4.4	276760
0.001001	232416	231604	230883	-672.5	+3.3	279015
0.10000	210945	209807	208688	-1088.0	+1.6	279355

Although of the same order of magnitude the values of  $(-\Delta H)$  are irregular. These irregularities are, however, within the limits of experimental error. The effects due to a simultaneous error of 0.10 m.v. at 25° and 35°, respectively, have been calculated. While a deviation of this magnitude causes a variation of only 0.005% in the value of  $(-\Delta F)$  it produces a change in the temperature coefficient ( $\alpha$ ) sufficient to produce an error of 2% in the value of the heat-content decrease.

**The Free-energy Decrease Accompanying the Transfer of One Mole of Potassium Bromide from Various Concentrations (c) to 0.10 M.—**

TABLE III.

THE FREE-ENERGY DECREASE ATTENDING THE TRANSFER OF ONE MOLE OF POTASSIUM BROMIDE FROM CONCENTRATION (c) TO 0.10 M.

c.	$(-\Delta F)_{25}$ joules.	$(-\Delta F)_{15}$ joules.	$(-\Delta F)_{35}$ joules.
2.8032	15689	15961	16241
1.03486	10315	10479	10703
0.51048	7266	7411	7508
0.25258	4120	4198	4323
0.10048	29	29	30
0.050184	-3127	-3174	-3239
0.010021	-11518	-10662	-10864
0.005009	-13808	-14015	-14193
0.001001	-21471	-21797	-22193

From the free-energy decrease attending the cell reaction at the various concentrations we can now obtain, by subtraction, the free-energy decrease attending the transfer of one mole of potassium bromide from a solution of any given concentration to one exactly 0.1 *M*. These values expressed in joules are given in the accompanying table.

**Measurement of Concentration Cells without Ion Transference.—**

(B).  $\text{Ag} \mid \text{AgBr}, \text{KBr} (c_1) \mid \text{K.Hg}_x - \text{Hg}_x.\text{K} \mid \text{KBr} (c_2), \text{AgBr} \mid \text{Ag}.$

(C).  $\text{K.Hg}_x \mid \text{KBr} (c_1), \text{AgBr} \mid \text{Ag} - \text{Ag} \mid \text{AgBr}, \text{KBr} (c_2) \mid \text{Hg}_x.\text{K}.$

The particular construction of the cell used rendered easy and convenient the determination of the electromotive forces of cells of both types, (B) and (C). In every set-up a complete set of readings was made on each type of cell and the potentials compared. Since the electromotive force of either of these cells depends, at any given temperature, solely upon the logarithms of the ratios of the activity products of the two ions at the molal concentrations ( $c_1$ ) and ( $c_2$ ), the electromotive forces of (B) and (C) should be identical. The mean potentials of each of the two types do not in any case differ by more than 0.03 m.v. For this reason we have entered in Table IV only those potential readings derived from Cell B. These data are easily reproducible and are accurate to 0.03 m.v.

TABLE IV.  
ELECTROMOTIVE FORCES OF CONCENTRATION CELLS WITHOUT ION TRANSFERENCE.

$c_1$ .	$c_2$ .	$E_{25}$ volts.	$E_{30}$ volts.	$E_{35}$ volts.
2.8032	0.25258	0.11976	0.12194	0.12415
1.03486	0.10048	0.10672	0.10861	0.11049
0.51048	0.10048	0.07514	0.07643	0.07772
0.25258	0.10048	0.04263	0.04336	0.04408
0.51048	0.050184	0.10732	0.10914	0.11096
0.10048	0.010021	0.10892	0.11078	0.11268
0.050184	0.005009	0.11064	0.11251	0.11442
0.010021	0.001001	0.11346	0.11538	0.11732

**The Free Energy of Dilution and the Decrease in Heat Content Attending the Transfer of One Mole of Potassium Bromide from Concentration  $c_1$  to  $c_2$ .—**The decrease in free energy, expressed in joules, attending the transfer of one mole of potassium bromide from concentration  $c_1$  to concentration  $c_2$  has been obtained by multiplying the electromotive force of the cell by 96494. These results together with the temperature coefficients of free energy decrease are given in Table V. The values for the decrease in heat content attending the same transfer have also been calculated and are included in the same table. The value of  $\alpha$ , if potassium bromide behaved as a perfect solute, would be 0.003353. The corresponding decrease in heat content is zero. While these theoretical values are approached it will be observed that even at the highest dilutions employed potassium bromide does not behave as a perfect solute.



TABLE V.

THE FREE ENERGY OF DILUTION AND THE HEAT-CONTENT DECREASE ATTENDING THE TRANSFER OF ONE MOLE OF POTASSIUM BROMIDE FROM CONCENTRATION  $c_1$  TO  $c_2$ .

$c_1$ .	$c_2$ .	$(-\Delta F)_{25}$ joules.	$(-\Delta F)_{10}$ joules.	$(-\Delta F)_{35}$ joules.	$\alpha \times 10^4$ .	$\beta \times 10^4$ .	$(-\Delta H)_{25}$ joules.
2.80320	0.25258	11556	11767	11980	+3617	+3.0	-896
1.03486	0.10048	10298	10480	10662	+3551	-1.8	-602
0.51048	0.050184	10356	10531	10707	+3382	+0.4	-84
0.10048	0.010021	10510	10690	10873	+3380	+6.0	-79
0.050184	0.005009	10676	10957	11041	+3365	+7.0	-41
0.010021	0.001001	10947	11133	11320	+3360	+3.6	-37

**Measurements of the Cells with Ion Transference.**— $\text{Ag} | \text{AgBr}, \text{KBr} (c_1) | \text{KBr} (c_2), \text{AgBr} | \text{Ag}$ . The cells with ion-transference employed in this work were made by joining two of the half-cells containing silver bromide electrodes by a flowing-junction device similar to that described and used by Lamb and Larson.<sup>13</sup> This arrangement gave results that were easily reproducible to 0.03 m.v. Table VI contains a summary of these results.

TABLE VI.

ELECTROMOTIVE FORCES OF CELLS WITH ION TRANSFERENCE.

$c_1$ .	$c_2$ .	$E_{25}$ volts.	$E_{10}$ volts.	$E_{35}$ volts.
2.8032	0.25258	0.05811	0.05928	0.06073
1.03486	0.10048	0.05237	0.05341	0.05443
0.51048	0.050184	0.05311	0.05406	0.05498
0.10048	0.010021	0.05394	0.05487	0.05587
0.05018	0.005009	0.05491	0.05582	0.05682
0.01002	0.001001	0.05627	0.05731	0.05834

**The Transference Numbers of the Potassium Ion.**—Thermodynamically the electromotive force of a concentration cell with ion transference is given by the relation:

$$E_t = \frac{N_K RT}{F} \ln \frac{C_1^2 \cdot \alpha_1^+ \cdot \alpha_1^-}{C_2^2 \cdot \alpha_2^+ \cdot \alpha_2^-},$$

where  $N_K$  represents the transference number of the potassium ion,  $(\alpha_1^+, \alpha_1^-)$  and  $(\alpha_2^+, \alpha_2^-)$  are the activity coefficients of the ions at concentrations  $c_1$  and  $c_2$ , respectively.

The corresponding expression for the electromotive force of a cell without ion-transference is

$$E = \frac{RT}{F} \ln \frac{C_1^2 \cdot \alpha_1^+ \cdot \alpha_1^-}{C_2^2 \cdot \alpha_2^+ \cdot \alpha_2^-}.$$

The ratio,  $\frac{E_t}{E} = N_K$ , gives us directly the transference number of the potassium ion. These values are recorded in Table VII. From these results it is to be observed that dilution is accompanied by a slight but

<sup>13</sup> Lamb and Larson, THIS JOURNAL, 42, 229 (1920).

gradual increase in the transference number. The effect of temperature change is practically negligible between 25° and 35°.

TABLE VII.  
TRANSPERANCE NUMBER OF THE POTASSIUM ION.

$c_1$	$c_2$	$(N_K)_{25}$	$(N_K)_{30}$	$(N_K)_{35}$
2.8032	0.25258	0.485	0.486	0.489
1.03486	0.10048	0.491	0.492	0.493
0.51048	0.050184	0.495	0.495	0.496
0.10048	0.010021	0.495	0.496	0.496
0.050184	0.005009	0.496	0.496	0.497
0.010021	0.001002	0.496	0.497	0.497

**The Activity Coefficients of the Ions.**—From the observed electromotive forces, Table IV, it is possible to calculate, by adding algebraically, the electromotive force of a cell containing any two of the concentrations employed in this work. In this manner the electromotive forces given in the following table have been computed. If now we make the assumption that at 0.001001  $M$  (0.001  $N$ ), the activity of the ions is equal to their concentration, as determined from conductance measurements, the product of the activity coefficients,  $\alpha_K + \alpha_{Br^-}$ , at any other concentration can be calculated directly. These values, thus calculated, are given in Table VIII.

TABLE VIII.  
THE ELECTROMOTIVE FORCES OF CONCENTRATION CELLS INVOLVING EACH CONCENTRATION ( $c$ ) WITH 0.0010017  $M$  AND THE ACTIVITY COEFFICIENT PRODUCTS AT THE CONCENTRATION ( $c$ ).

$c$	$E_{25}$	$(\alpha_K + \alpha_{Br^-})_{25}$
2.8032	0.38447	0.3625
1.03486	0.32910	0.3390
0.51048	0.29752	0.3945
0.25258	0.26501	0.4690
0.10048	0.22238	0.5510
0.050184	0.19020	0.6245
0.010021	0.11346	0.7914
0.005009	0.07956	0.8493
0.001001	0.00000	0.9565

In their study of the activity of largely ionized substances, Noyes and MacInnes<sup>3</sup> have computed from electromotive-force data the mean activity coefficients of the ions of potassium hydroxide, potassium chloride, lithium chloride and hydrochloric acid. Since for any given concentration the potassium and chloride ions are assumed to possess equal activities, the mean activity coefficients for this salt may be considered as the activity coefficient of either of its ions. If now we assume that at any given concentration the activity of the potassium ion is a constant and independent of the anion associated with it, we are in a position to calculate the activity of the bromide ion. In order to make these calculations the values of

$\alpha_{K^+ \cdot Br^-}$ , (Table VIII), were plotted on a large scale against the logarithms of the concentrations. From the curve thus obtained the values of  $\alpha_{K^+ \cdot Br^-}$  corresponding to round concentrations were then read. These activity coefficient products were then divided by the value of  $\alpha_{K^+}$  for potassium chloride at the same concentration, taken from the data of Noyes and MacInnes.<sup>3</sup> The quotients obtained are obviously the activity coefficients of the bromide ion.

The results of these computations are summarized in Table IX. The second column contains the values of  $\alpha_{K^+} = \alpha_{Cl^-}$  taken from the data of Noyes and MacInnes. Col. 3 contains the values of  $\alpha_{K^+ \cdot Br^-}$  read from the curve, while Col. 4 contains the values of  $\alpha_{Br^-}$  calculated in the manner described in the preceding paragraph. The values given in the fifth column are the values of  $\alpha_{Br^-}$  calculated in a similar manner from the data of Lewis and Storch.<sup>14</sup>

TABLE IX.  
THE ACTIVITY COEFFICIENTS OF THE IONS AT ROUND CONCENTRATIONS.

C.	$\alpha_{K^+} = \alpha_{Cl^-}$	$\alpha_{K^+ \cdot Br^-}$	$\alpha_{Br^-}$	$\alpha_{Br^-}$
2.800	.....	0.3625	0.602	.....
1.000	0.593	0.3440	0.579	.....
0.700	0.618	0.3788	0.613	.....
0.500	0.638	0.4045	0.634	.....
0.300	0.673	0.4525	0.672	.....
0.100	0.745	0.5540	0.743	0.742
0.050	0.790	0.6260	0.792	.....
0.030	0.823	0.6785	0.824	0.822
0.010	0.890	0.7930	0.891	0.886
0.005	0.923	0.8520	0.922	.....
0.003	0.943	0.8885	0.942	.....
0.001	0.979	0.9565	0.978	.....

A glance at the above table shows conclusively that at equal molal concentrations, at least up to 0.5 *M*, the activity coefficients of the chloride and bromide ions are identical. Furthermore, the close agreement between the values of the activity coefficients of the bromide ion computed from the data for potassium bromide and those calculated from the data for hydrogen bromide is further evidence of the independent activity of the individual ions.

Since the completion of the experimental part of this paper there has appeared an article by Lewis and Randall<sup>15</sup> on the activity coefficients of strong electrolytes. Using the data of Bates and Kirschmann<sup>16</sup> on the partial vapor pressures of the hydrogen halides, Lewis and Randall have arrived at the same conclusion regarding the activity coefficients of the

<sup>14</sup> Lewis and Storch, *THIS JOURNAL*, **39**, 1544 (1917).

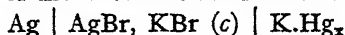
<sup>15</sup> Lewis and Randall, *ibid.*, **43**, 1112 (1921).

<sup>16</sup> Bates and Kirschmann, *ibid.*, **41**, 1991 (1919).

chloride, bromide and iodide ions. These results indicate further that the differences observed in the activity of the various uni-univalent halides, when at the same concentration, are due primarily to differences in the activity of the cations.

### Summary.

1. Measurements of the electromotive forces of the cells



have been made.

2. The free-energy decrease and the decrease in heat content attending the reaction in these cells have been calculated.

3. The free energy decrease attending the transfer of one mole of potassium bromide from various concentrations ( $c$ ) to 0.10  $M$  have been computed.

4. The electromotive forces of concentration cells with ion transference and without ion transference have been measured. From these values the transference numbers of the potassium ion have been calculated.

5. The free-energy decrease and the heat-content decrease accompanying the transfer of one mole of potassium bromide from concentration  $c_1$  to concentration  $c_2$  have been computed.

6. The activity coefficients of the bromide ion have been calculated and a comparison made of the activity coefficients of the chloride and bromide ions. For all concentrations up to 0.5  $M$  the activity coefficients of these two ions are practically equal.

IOWA CITY, IOWA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD COLLEGE AND OF SIMMONS COLLEGE.]

## THE SOLUBILITY OF SILVER CHLORIDE IN DILUTE CHLORIDE SOLUTIONS AND THE EXISTENCE OF COMPLEX ARGENTICHLORIDE IONS. II.<sup>1</sup>

BY GEORGE SHANNON FORBES AND HARRIET ISABELLE COLE.

Received August 12, 1921.

In a previous paper by one of us,<sup>2</sup> where earlier work on this subject was discussed, the solubility of silver chloride in concentrated chloride solutions was proved proportional to integral powers of chloride concentration. From these results was inferred the existence of the complex ion  $\text{AgCl}_4^=$  in the higher concentrations, and of  $\text{AgCl}_3^=$  in the range from 1.5  $N$  down to 0.5  $N$ . Below that point, however, the constant indicating the latter ion increased, which suggested that the ion  $\text{AgCl}_2^-$  might predominate at the lowest concentrations.

<sup>1</sup> This work was performed in 1915, at Simmons College.

<sup>2</sup> See Forbes, *THIS JOURNAL*, 33, 1937 (1911).

The present paper records an effort to investigate solutions less than normal in chloride, which necessitated the measurement of solubility to 0.05 mg. per liter.

Sodium and potassium chlorides were precipitated by hydrogen chloride, washed, dried and ignited. Other salts were recrystallized from redistilled water, and made up into concentrated stock solutions. Silver nitrate solution, 0.001 *N*, was similarly prepared. Portions of the stock solutions were weighed from weight burets and analyzed with the customary precautions, including careful standardization of weights. The greatest variation between duplicate analyses was 6 parts in 10,000.

An 800cc. deep-form beaker was weighed clean and dry with a glass stirrer. The desired amount of solid salt or of stock solution was weighed out, and the volume made up to about 500 cc. with redistilled water carefully protected from dust. The beaker was brought to 25.0° in a thermostat electrically regulated to 0.05°. It was then placed in a blackened wooden box with a comparison beaker containing a similar solution. On the other side of the glass partition was placed a 300-watt tungsten lamp. Black rings at the tops and bottoms of the beakers excluded annoying reflections. If both beakers were equally free from opalescence, a quantity of 0.001 *N* silver nitrate known from preliminary experiments to be just insufficient to cause opalescence was run into the first beaker with vigorous stirring. After an hour at 25°, which had been proved enough to develop opalescence if it was to appear at all, the beaker was carefully wiped, and once more examined in the modified nephelometer, to prove the continued absence of precipitate. Two drops of the silver solution, or 5 in the most concentrated solutions, were added, with vigorous stirring, and the beaker returned to the thermostat for another hour, after which it was again examined and so on. It appeared improbable that supersaturation would greatly exceed the last addition of silver nitrate, about  $6 \times 10^{-8}$  mole in 500 cc. in this case.<sup>3</sup> When opalescence appeared, the total weight of the solution was at once determined, also its density by pycnometer. The concentrations in the solution at the end-point could then be calculated without uncertainty due to evaporation or change in volume on mixing. The results appear in Tables II to IV.

The total silver present at the end-point may be classified as follows: (a) silver ion, (b) dissolved molecules of silver chloride, supersaturated or unsaturated, (c) precipitated silver chloride, and colloid in dispersion not too high to be seen under the given light conditions, (d) silver chloride in complex ions and molecules, and possibly adsorption complexes of colloidal silver chloride too highly dispersed to be visible under the given light conditions.

Assuming the solubility product to be  $2 \times 10^{-10}$ , the  $(\text{Ag}^+) = 2 \times 10^{-10} / (\text{Cl}^-)$ . As this correction is in all the cases less than  $3 \times 10^{-8}$  mole in 500 cc. it will be neglected for the moment.

<sup>3</sup> Compare Ref. 2, p. 1939.

The working hypothesis was now tried that the silver chloride in the conditions (b) and (c), under the constant experimental conditions, made up a constant total which may be expressed as  $b$ . Let us also postulate

TABLE I.

EVALUATION OF  $b$  FOR SODIUM CHLORIDE.Let  $b = \text{AgCl as Dissolved Molecules} + \text{Colloidal} + \text{Precipitated}$ .

$$k_1 = \frac{\text{total silver}_1 - b}{\text{total chloride}_1} = \frac{\text{total silver}_2 - b}{\text{total chloride}_2}$$

Total chloride.	Total silver.	$b$ .	Total chloride.	Total silver.	$b$ .
{ 3.86	0.00072	0.00058	{ 17.58	0.00131	0.00077
{ 9.24	0.00091		{ 36.54	0.00189	
{ 17.58	0.00131	0.00047	{ 88.44	0.00361	0.00068

Average = 0.00063

that (complex silver) = (total silver -  $b$ ). If it be further assumed that the complex radical in dilute solutions is  $\text{AgCl}_2$ , then  $(\text{AgCl}_2) = k_1$  (total chloride). Combining, (total silver -  $b$ ) =  $k_1$  (total chloride). The two unknowns,  $b$  and  $k_1$  may now be evaluated by solving at any two concentrations, but pairs of concentrations below 0.1  $N$ , where  $b$  is not small in comparison with total silver, and where the complex is sharply defined, promise the best results. Table I shows 4 values of  $b$  thus determined for sodium chloride with an average of 0.00063, while 5 similar pairs with hydrochloric acid yielded 0.00061. The closeness of the agreement, though in the main accidental, does yet in some measure justify the assumption made.

The total silver present in complex form, and the values of  $k_1$  are given in Tables II to IV. The value of  $k_1$  varies without definite trend up to 0.1  $N$ , after which it tends to increase rapidly, while  $k_2$ , calculated on the assumption that the complex radical is  $\text{AgCl}_3$ , approaches constancy as shown in the previous paper. Table IV, in which total chloride is constant, shows substantially the same effects of the positive radical

TABLE II.

SILVER CHLORIDE IN SODIUM CHLORIDE SOLUTIONS.

Concentrations in Milli-equivalents per liter.

 $b = 0.00063$ .

Total NaCl.	Total silver.	Total complex.	$k_1 \times 10^4$ .	$k_2 \times 10^2$ .
3.86	0.00072	0.00009	0.23	....
9.24	0.00091	0.00028	0.30	....
17.58	0.00131	0.00068	0.39	....
36.54	0.00189	0.00126	0.35	....
88.44	0.00361	0.00298	0.34	3.84
355.6	0.0174	0.0168	0.47	1.32
511.2	0.0280	0.0274	0.54	1.06
974.7	0.0806	0.0801	0.82	0.84

on  $k_1$  which were noted at higher concentrations. Where  $b$  was not evaluated, it was taken as the mean of 0.00063 and 0.00061. The value of  $k_1$  for hydrochloric acid, which seems to be exceptional, is much higher than its neighbors in Table III.

TABLE III.  
SILVER CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS.  
Concentrations in Milli-equivalents per Liter.  
 $b=0.00061$ .

Total HCl.	Total silver.	Total complex.	$k_1 \times 10^4$ .	$k_2 \times 10^7$ .
4.78	0.00075	0.00014	0.29	....
9.38	0.00084	0.00023	0.25	....
17.8	0.00125	0.00064	0.36	....
34.1	0.00219	0.00158	0.46	....
74.1	0.00361	0.00300	0.41	....
91.4	0.00426	0.00365	0.40	4.38
316.7	0.01403	0.01342	0.42	1.32
681.8	0.0448	0.0442	0.64	0.94
779.7	0.0559	0.0553	0.71	0.91
925.8	0.0719	0.0713	0.77	0.83

TABLE IV.  
VALUES OF  $k_1$  IN 0.35 *N* CHLORIDE SOLUTIONS.  
Concentrations in Milli-equivalents per Liter.

Chloride taken.	Total chloride.	Total silver.	$b$ .	Total complex.	$k_1 \times 10^4$ .
HCl	34.1	0.00219	0.00061	0.00158	0.44
NaCl	36.5	0.00189	0.00063	0.00126	0.35
NH <sub>4</sub> Cl	37.4	0.00162	0.00062	0.00100	0.27
KCl	36.7	0.00172	0.00062	0.00110	0.30
RbCl	37.7	0.00181	0.00062	0.00119	0.32
CaCl <sub>2</sub> /2	38.6	0.00175	0.00062	0.00113	0.29
SrCl <sub>2</sub> /2	36.9	0.00172	0.00062	0.00110	0.30
BaCl <sub>2</sub> /2	37.5	0.00157	0.00062	0.00095	0.25

The effects of sodium nitrate, nitric acid, and alum, are shown in Table V. The metathetical action of sodium nitrate is always obvious,<sup>4</sup> though

TABLE V.  
OTHER ELECTROLYTES ADDED TO SODIUM CHLORIDE.  
Concentrations in Milli-equivalents per Liter.

Total NaCl.	Added electrolyte.	Conc. added.	Total silver.	Difference fr. pure NaCl.
4.26	.....	...	0.00077	.....
4.37	NaNO <sub>3</sub>	45	0.00102	+0.00025
4.37	HNO <sub>3</sub>	200	0.00099	+0.00022
36.54	.....	...	0.00189	.....
36.53	NaNO <sub>3</sub>	360	0.00220	+0.00031
35.41	HNO <sub>3</sub>	200	0.00160	-0.00029
37.83	Alum	6	0.00189	=0.00000

<sup>4</sup> Richards and Wells, *Carnegie Inst. Pub.*, 28, 29 (1905).

one of the results with nitric acid, doubtless erroneously, indicates a decrease in solubility. A trace of alum is without effect, which suggests that colloid formation is relatively unimportant under the given conditions.

The "activity" conception of G. N. Lewis and others was duly considered before presenting these results. In the previous paper it was shown that complex formation in hydrochloric acid at higher concentrations, at least, is always less than in sodium chloride. The activity of hydrochloric acid, however, always exceeds that of sodium chloride, and at 5 *N* it is 5 times as great.<sup>5</sup> The quantitative application of the activity principle must therefore be postponed. In the present work, also, it was found that *b* and *k* were more constant if total chloride concentrations were used without correction for either ionization or activity coefficient. Possibly chloride molecules, as well as chloride ions, operate to form complexes. At first sight, this seems inconsistent with the observation in the previous paper that the feebly ionized zinc chloride shows but little tendency to form the argentichloride complex. But here self-complex formation, as  $\text{ZnCl}_2 + 2\text{Cl}^- = \text{ZnCl}_4^{2-}$  is no doubt considerable.

In very dilute solutions, the total concentration of silver in "true solution" exclusive of the constant *b* should equal the sum of silver ion and of argentichloride ion per liter, *i. e.*,  $2 + 10^{-10}/(\text{MCl}) + k_1(\text{MCl})$ . By "true solution" is meant one optically clear under the light conditions described above, and one doubtless filterable without loss through a filter paper or Gooch crucible. Differentiating total silver with respect to chloride concentration, we find that the condition under which the derivative becomes zero is  $(\text{MCl})^2 = 2 \times 10^{-10}/k_1$ . Using  $0.34 \times 10^{-4}$  as the average value of *k*<sub>1</sub> the minimum total concentration of silver in true solution should be found at 0.0025 *N*, instead of at 0.01 *N*, as predicted in the previous paper under the assumption that the complex radical  $\text{AgCl}_2$  persisted in the most dilute solutions. At 0.0025 *N*,  $2 \times 10^{-10}/(\text{MCl}) = 8 \times 10^{-8}$  and  $k(\text{MCl}) = 8 \times 10^{-8}$ , by a curious coincidence. The total silver concentration exclusive of the constant *b* is therefore  $1.6 \times 10^{-8}$  mole, or 0.000025 gram per liter. According to the present work, no chloride solution can contain less than this amount of silver chloride per liter in true solution, if just a bare trace of freshly precipitated silver chloride is present.

At first sight, the results of this paper might seem in preposterous disagreement with those of Richards and Wells, who found a solubility of 0.000003 g. per liter<sup>6</sup> in a solution containing perhaps an excess of 0.1 equivalent of chloride per liter. It should be emphasized, however, that these determinations were made in filtrates from large precipitates of silver chloride, whose enormous surfaces may have occluded or adsorbed the com-

<sup>5</sup> Lewis and Randall, *THIS JOURNAL*, 43, 1117, 1123 (1921).

<sup>6</sup> Richards and Wells, *Ref. 4*, p. 30.



plex most obstinately. Indeed, these authors suggest that even glass might adsorb sufficient silver chloride to account for losses observed on standing.<sup>7</sup> Another possibility is that chloride solutions, in the absence of much adsorbing solid, peptize silver chloride in a strictly reproducible fashion.<sup>8</sup> If so, the degree of dispersion must be very high. The possibility that more than one form of silver chloride with different solubilities may exist, is not excluded. The behavior of silver chloride is so variable under changing conditions that even the above noted difference is not disconcerting, though it invites further investigation.

### Summary.

To various chloride solutions less than 0.1 *N* in concentration, 0.001 *N* silver nitrate solution was added to incipient precipitation, at 25°. The total silver was invariably given by the sum:  $2 \times 10^{-10}/(\text{MCl}) + 3.4 \times 10^{-5}(\text{MCl}) + b$ , where  $2 \times 10^{-10}$  is the solubility product,  $3.4 \times 10^{-5}$  a constant possibly connected with a complex of the type  $\text{AgCl}_2$ , and *b* apparently is the constant sum of silver chloride in precipitate, in dispersion, and in dissolved molecules. The great difference between this observed total and the minute silver content of filtrates from large precipitates of silver chloride is discussed.

Silver chloride should be most insoluble, at 25°, in 0.0025 *N* chloride solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY.]

## THE USE OF THE WATER INTERFEROMETER AS A PRESSURE GAGE.<sup>1</sup>

BY L. VAN DOREN, H. K. PARKER AND P. LOTZ.

Received August 18, 1921.

Nitrogen-filled glass manometers have been used in this laboratory for many years for the measurement of osmotic pressure, although there are certain objections to their use for this purpose; and since it was desired to measure pressures greater than they could withstand (about 100 atmospheres) it was necessary to devise a suitable manometer for this purpose. Frazer and Myrick<sup>2</sup> by use of a resistance pressure gage were able to measure osmotic pressure of concentrated sucrose solutions with approximately the same sensitivity at all pressures, but here also,

<sup>1</sup> Richard and Wells, Ref. 4, p. 29.

<sup>2</sup> See Homochemical Compounds, V. Veimarn, *Kolloid Z.*, **28**, 97 (1921).

<sup>1</sup> This work was assisted by grants from the Carnegie Institution of Washington, and was carried out at the suggestion of J. C. W. Frazer.

<sup>2</sup> Frazer and Myrick, *THIS JOURNAL*, **38**, 1907 (1916).

due to hysteresis effects in the resistance coils and consequent shifting of the zero, the method was not entirely satisfactory. The construction of the apparatus described below which is devoid of these objections, is believed to be satisfactory for this purpose and may also have other similar applications.

The instrument is a modification of the Zeiss water interferometer. Instead of using this instrument in a method for the analysis of solutions it is here used to measure pressure differences.

Figs. 1a and b show respectively the construction of the Zeiss water interferometer and its modifications for use as a pressure gage. In the Zeiss instrument white light from a slit is made parallel by a collimating lens, *L*, and passes through the rectangular openings *R*<sub>1</sub>, *R*<sub>2</sub> as two beams, which, reflected from the mirror, *M*, pass back and unite at

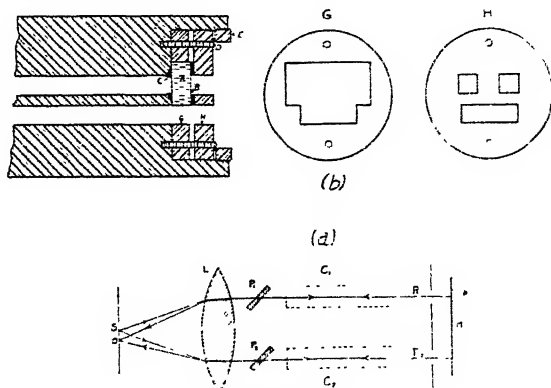


Fig. 1.

*O* forming a system of interference fringes and are viewed by a suitable eye-piece. The similar chambers *C*<sub>1</sub>, *C*<sub>2</sub>, are placed, one in the path of each beam. When the optical paths are different, as is the case when one of the chambers contains the pure solvent and the other a solution, the interference fringes are displaced to a position at the left or right of *O*. The displacement is compensated by means of the inclined plate *P*<sub>1</sub>, *P*<sub>2</sub> being fixed. The measurement of the amount of adjustment of *P*<sub>1</sub> necessary to bring back the central bright fringe to the zero position is used as a means of analyzing a solution for a single variable component or several mutually dependent components. The water interferometer adapts itself readily to use as a pressure gage by simply altering the cells *C*<sub>1</sub>, *C*<sub>2</sub> in such a way that the water contained in one of them is kept under atmospheric pressure while that in the other is subjected to the pressure to be determined. For this purpose the cells *C*<sub>1</sub>, *C*<sub>2</sub> are replaced by pressure chambers. These are parallel holes about 6.25 mm. in diameter bored through a solid bronze cylinder and fitted at each end with heavy plate-glass windows *A*, Fig. 1b. Just beneath the pressure chambers the bronze cylinder is provided with a longitudinal slot for beams of light which form the stationary bands of reference.

When pressure is applied to the water in one of the chambers its refractivity is increased and the interference fringes are displayed. The adjustable plate mentioned above enables one to compensate for this

displacement, and it is readily seen that such an instrument after having been calibrated may be used for the measurement of any pressure within the range of adjustment covered by the movable plate.

The chief difficulty to be overcome was to obtain a tight joint between the plate glass windows and the pressure chamber. Fig. 1b shows the construction of one end of the bronze block. A washer C was cut from 3 mm. soft sheet rubber with beveled sides so as to fit the countersunk end of the pressure chamber. This washer is cut slightly oversize, thus giving good contact and insuring a tight joint. A dilute solution of rubber is spread around the washer and hole of the non-pressure chamber, which is not countersunk and requires no washer as no pressure is developed in this chamber.

After assembling and allowing the solvent to evaporate, the chamber is dried thoroughly and a slow stream of gaseous sulfur chloride is blown into the chambers for 10 minutes. This operation vulcanizes the rubber to the required hardness. The glass plate is held in place by a brass plate G, of the same thickness and cut to fit the glass plate snugly. The latter is held tightly against the end of the chamber by a similar brass plate H on which a washer B, made of asbestos and rubber, is placed to take up any unevenness in the glass. Finally, pressure is brought to bear on H by a screw collar E. Some difficulty was experienced in obtaining a suitable washer material to place between the glass and the outside brass plate. When soft thin rubber washers were used the pressure caused them to flow from the small brass section between the pressure chamber and the opening below, thus leaving the glass plate unevenly supported and causing leaks. When harder materials, as leather, were used the windows were frequently broken when pressure was applied. The packing which was successful is used in steam packing and for gaskets and is sold under the trade name of "Durabla Packing." It answered our purpose in having sufficient resilience to take up any unevenness, possessing no tendency to flow, and not requiring any take-up after pressure is applied.

### Increased Range of the Interferometer.

On calibration, the pressure limit of the apparatus, was found to be approximately 60 atmospheres. It was therefore found necessary to devise some means by which the range of the instrument could be increased. This was accomplished by inserting a thin glass plate in the path of the beam passing through the non-pressure chamber, the glass plate being of such thickness that, when inserted, it would compensate for approximately 60 atmospheres. With this plate inserted we thus had a range of from 60 to 120 atmospheres, approximately. The final adjustment for reading is accomplished by the usual method of tilting the glass plate of the interferometer. Thus, by making up several slides with plates of increasing thickness we were able to extend the range of the apparatus to any pressure required.

The glass plates were attached firmly to brass frames by Canada balsam, the plates being machined to fit into slides attached to the water bath of the interferometer.

We found that thin microscope-cover plates were quite regular in thickness and proved easily adaptable to the problem at hand. The plates used varied in thickness from 0.1016 to 0.3556 mm.

The method of mounting these thin glass plates was such that they

could be replaced in exactly the same position and thus any error that would arise from any slight irregularity in the plate was avoided.

### Calibration of Apparatus.

The apparatus was calibrated against an absolute pressure gage in the Geophysical Laboratory.<sup>3</sup> The calibration was made at both 20° and 30°. In the data for Plate 6 it was found necessary to read a different band as our zero point at 30° than was read at 20°, hence the apparent discrepancy in the calibration for this plate. The personal equation in reading the interferometer as used for pressure measurements is considerable but care was taken to calibrate in the same manner as when using the instrument for the measurement of pressure. This instrument has been used satisfactorily for the direct measurement of osmotic pressure as described in the following article.

TABLE I.  
CALIBRATION DATA.

Absolute gage pressure in atmospheres.	Reading on interferometer.			Reading on interferometer.		
	30°.			20°.		
	1.	2.	Mean.	1.	2.	Mean.
	Interferometer Alone.					
24.1	1116	1114	1115	1170	1178	1174
36.6	1759	1752	1756	1807	1808	1808
49.0	2413	2406	2410	2504	2508	2506
55.3	2789	2782	2786	2888	2893	2890
	Plate 6.					
55.3	209	206	207	207	209	208
74.1	1092	1092	1092	1087	1092	1089
102.2	2552	2552	2552	2611	2603	2607
	Plate 3.					
114.6	49	43	46	240	244	242
139.7	1209	1202	1206	1410	1420	1415
167.2	2639	2649	2644	2927	2934	2930
	Plate 8.					
154.7	-296	-297	-297	-57	-63	-60
167.2	254	250	252	480	488	484
192.2	1444	1444	1444	1677	1672	1674
213.8	2537	2535	2536	2846	2854	2850
	Plate 7.					
220.0	.....	.....	.....	-165	-175	-170
244.9	.....	.....	.....	963	928	932
269.8	.....	.....	.....	2180	2180	2180

The difference in the readings at 20° and 30° shows that at a higher temperature the effect of increased pressure on the refractive index diminishes and the magnitude of the difference found by the authors is in

<sup>3</sup> The authors wish to express their thanks for the courtesies extended them by members of the staff of the Geophysical Laboratory.

agreement with the work of Röntgen and Zehnder<sup>4</sup> who measured the effect of temperature on the pressure coefficient of the refractive index. One may also determine from the calibration data above the extent to which the temperature of the instrument must be controlled in order to secure the desired accuracy.

BALTIMORE, MARYLAND.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY.]

## THE OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS OF SUCROSE AS DETERMINED BY THE WATER INTERFEROMETER.

BY PAUL LOTZ AND J. C. W. FRAZER.

Received August 18, 1921.

Many difficulties are encountered in the direct measurement of the osmotic pressures of solutions among which are those involved in measuring the pressure. The limit of pressure that the glass manometer will stand as found by Frazer and Myrick is about 100 atmospheres. Among the uncertainties involved in the use of gas manometers are the deviation of gases from Boyle's law, and the fact that gas may be occluded between the mercury and the glass, both of which may become appreciable when measuring high pressures. The percentage error involved in reading the levels of the mercury menisci also increases with the compression of the gas and the change of form of the meniscus is not to be disregarded. So the higher the pressure the less accurate the gas manometer becomes.

Frazer and Myrick<sup>2</sup> by the use of the resistance pressure gage were able to obtain a constant sensitivity at all pressures, but owing to certain difficulties such as hysteresis in the resistance coils it was thought wiser to seek a method for measuring high pressures that would be less objectionable.

Berkeley and Hartley<sup>3</sup> determined the osmotic pressure of several solutions up to pressures of 133 atmospheres by applying mechanical pressure and determining the equilibrium pressure by noting the point at which the solvent just ceases to pass through the semipermeable membrane.

In an article by Woods<sup>4</sup> the objection is raised that the osmotic pressure of solutions as measured is not the true osmotic pressure, but of that layer of solutions in immediate contact with the semipermeable membrane

<sup>4</sup> Röntgen and Zehnder, *Wied. Ann.*, 44, 34 (1891).

<sup>1</sup> This work has been assisted by grants from the Carnegie Institution of Washington.

<sup>2</sup> Frazer and Myrick, *THIS JOURNAL*, 38, 1907 (1916).

<sup>3</sup> Berkeley and Hartley, *Phil. Trans.*, 206A, 486 (1906).

<sup>4</sup> Woods, *Trans. Faraday Soc.*, 11, 29 (1915).

which is more concentrated than the solution proper, due to adsorption. This criticism applies more particularly to dilute solutions and has been partly answered by the work of Minter and Frazer.<sup>5</sup> They used a stirring device which could be operated during the time the measurements were being made.

The same osmotic pressure was also obtained by allowing the pressure to rise by the diffusion of solvent through the membrane as was obtained by submitting the solution to a hydrostatic pressure greater than the equilibrium pressure, which latter pressure is reached by the removal of solvent from the solution through the membrane.

### Apparatus.

The water interferometer as adapted to the measurement of pressure<sup>6</sup> was used in this work for measuring the osmotic pressures developed. The cells used were made by the method of Frazer and Myrick,<sup>2</sup> the membrane of copper ferrocyanide being deposited on the outside. The container of bronze was also the same as used in the above work.

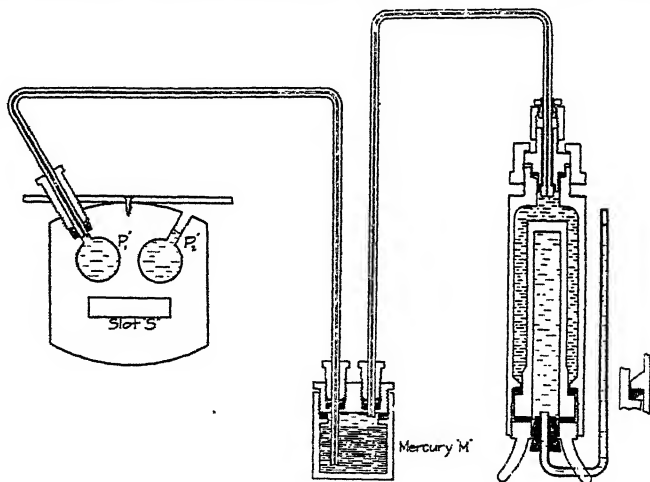


Fig. 1.

When attempting the measurements at  $55.7^\circ$  it was found necessary to modify the washer used between the cell shoulder and the cell container, due to the flowing of the rubber at this high temperature and pressure. This was prevented by inserting a bronze washer between the cell shoulder and washer as shown in insert Fig. 1.

### Temperature Control.

In the  $30^\circ$  experiments the entire apparatus was placed in a  $30^\circ$  air-

<sup>5</sup> Minter and Frazer, unpublished dissertation. Johns Hopkins University, 1917.

<sup>6</sup> Van Doren, Parker and Lotz, *THIS JOURNAL*, 43, 2497 (1921).

bath which varied but  $0.05^{\circ}$ . In the  $57.7^{\circ}$  experiments the cell and container were placed in a double-walled copper bath in which the constant temperature was maintained by boiling acetone in the outer compartment. The inner compartment containing the cell surrounded by water was cylindrical in shape, 10 cm. in diameter and 25 cm. high. With a bath of these small dimensions stirring was found unnecessary. Temperature varied from day to day about  $0.1^{\circ}$  with change in the atmospheric pressure but the time required to complete an experiment was very short, the maximum period required to obtain equilibrium being  $2\frac{3}{4}$  hours, in which interval no changes in temperature could be detected.

This form of apparatus fulfilled all expectations, proving convenient, strong, and of quick action, as the results in Table I show. Equilibrium was obtained in from 12 minutes for the lower concentrations to  $3\frac{3}{4}$  hours for the measurements at high concentrations. In the  $2 M$  measurements at  $55.7^{\circ}$  the final reading obtained after adjusting the apparatus was maintained throughout the experiment showing that equilibrium had been obtained even before the time recorded in the table.

In the  $30^{\circ}$  work all solutions used were at  $30^{\circ}$ , in the  $55.7^{\circ}$  work the solutions were cooled somewhat below  $55.7^{\circ}$  in order to lessen the effect of dilution of the solution being measured.

### Experimental.

**Preparation and Analysis of Solutions.**—Aqueous solutions of cane sugar were studied over the complete range of solubility. The sucrose used was carefully purified "rock candy." To facilitate ready comparison with previous work done in this laboratory, the solutions were all made up on the weight molar basis using atomic weights on the  $O = 16$  scale. The sugar in each instance was dissolved in distilled water made  $0.01 N$  with potassium ferrocyanide. The solvent against which the osmotic pressures were measured was  $0.01 N$  copper sulfate.

The extent to which the solutions were diluted during measurement was ascertained by the saccharimeter in the following manner. From the optical rotation, the concentration was determined by reference to a curve made by plotting the values of the ratios of the concentrations of the original solutions to their optical rotations against *their* optical rotations, *i. e.*, letting  $C$  represent the concentration, and  $r$  the optical rotation, the values of  $C/r$  were plotted against the values of  $r$ . By multiplying the optical rotation of a given solution by the corresponding value of  $C/r$  as determined from the curve, the concentration of the solution in grams of sugar for 1000 g. of water was obtained.

In the work on dilute solutions carried on in this laboratory, corrections for changes in concentration are made by changing the observed pressure the same percentage that the optical rotation of the solution changes during the measurement. This involves two errors, for it assumes that the change in optical rotation is linearly proportional to the change in concentration and that the osmotic pressure is a linear function of the concentration. The magnitude of the error may be negligible in the case of dilute solutions but in the case of concentrated ones the error would be

considerable. Hence in this work the final concentrations are determined from the curve described above and the observed osmotic pressures are recorded as the pressures of solutions of these concentrations.

The contents of the solvent compartment were examined after each experiment to determine to what extent the sugar had leaked through the membrane. The amount of sugar in the "solvent" could not be detected by the saccharimeter in any of our measurements except in Expt. 11. The cell used here was an old one that had not been used for several years and was set up without seasoning. All of the other cells used had been well seasoned at high pressures and gave very satisfactory results.

TABLE I.  
OSMOTIC PRESSURES.

Expt.	Sugar/1000 cc. of solution. G.	Sugar/1000 g. of water. G.	Equilibrium time. Min.	Osmotic pressure. Atmospheres.
30°.				
1	478.3	680	90	57.5
2	472.0	665	12	56.6
3	597.0	958	90	87.2
4	605.4	980	150	90.4
5	608.5	990	165	92.0
6	700.2	1260	195	129.5
7	695.0	1242	225	127.4
8	781.4	1549	180	169.1
9	781.4	1549	225	168.6
10	777.3	1533	90	164.1
11*	831.5	1758	300	198.2
12	826.2	1737	195	200.2
13	839.8	1796	165	206.1
55.7°.				
14	477.2	674	22	61.0
15	481.4	685	20	63.1
16	610.6	996	35	97.4
17	612.7	1000	16	98.7
18	702.3	1270	30	132.4
19	706.4	1284	55	133.5
20	732.5	1556	75	170.6
21	791.9	1590	90	178.7
22	856.5	1877	120	222.0
23	842.9	1810	135	213.8
24	900.2	2112	165	259.3
25	910.6	2190	135	265.6
26	No analysis.		135	273.0

\* Unseasoned Cell.

### Results.

Table I summarizes the experiments. Some were lost and not recorded, due to the washers breaking; and hence no analysis could be made of these solutions. In Expt. 26 the upper washer was broken and the ex-



periment was incomplete. No importance is attached to the result obtained in Expt. 11, as we found that the results obtained with unseasoned membranes as shown by solute leakage are invariably low and the true equilibrium pressure is not reached.

Frazer and Myrick report sugar leakage after reaching concentrations of 5 *M* and greater. We should therefore expect to find their results at these higher concentrations somewhat low. On plotting a curve with their results, *i. e.*, osmotic pressure against concentrations—a decided drop in the curve is noticed after passing 5 *M* concentrations. In comparing their results for corresponding concentrations with the results of Expts. 12 and 13 our predictions are found to be correct, since we obtained 200.2 and 206.1 as compared with 192.0 and 200.0, respectively, found by Frazer and Myrick.

The results obtained in this work for 6 *M* sucrose when substituted in the above curve of Frazer and Myrick give a continuous and regular curve at 30°.

In Fig. 2 the data in Table I are shown graphically. Here the concentration expressed in g. of sucrose for 1000 g. of water is plotted against the osmotic pressure in atmospheres. It will be noticed that the curve for 55.7° cuts the extrapolated 30° curve at a concentration of 2000 g. of sucrose to 1000 g. of water. Above this concentration the osmotic pressure of solutions at 55.7° is less than that of like concentration at 30°.

### Discussion.

Woods<sup>4</sup> calculated the value for osmotic pressure from the vapor-pressure measurements obtained by him for concentrated solutions of sucrose by using the Porter equation which connects the osmotic pressure and the vapor pressure of the solution and solvent. Data for 3 solutions of concentrations 92.0, 156.6 and 224.3 g. of sucrose to 100 g. of water respectively were obtained at temperatures from 60° to 90°.

He noticed that in the two more concentrated solutions the osmotic pressure as calculated showed a distinct tendency to diminish with rise in temperature.<sup>7</sup> The results obtained in this work indicate that, while

<sup>7</sup> Results obtained in this laboratory on sugar solutions up to *M* concentrations showed the same tendency, *i. e.*, to increase less than the theoretical value.

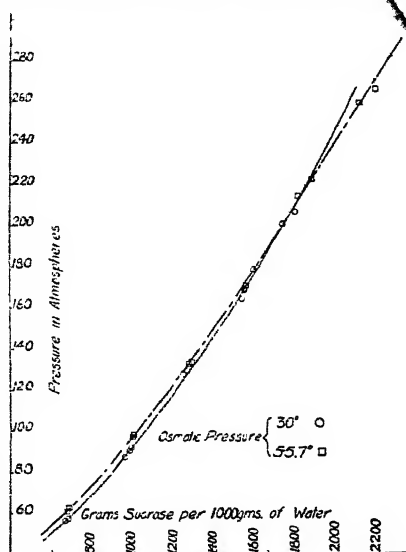


Fig. 2.

the calculated values obtained by Woods may be high, the relative values are not far from correct.

From a perfect solution the osmotic pressure would increase with rise in temperature according to the gas laws. Here, however, the increase is much less than the theoretical increase. This is quite evident even with the less concentrated solutions, while on approaching concentrations of 6 *M* the osmotic pressure at 55.7° becomes actually less than the values obtained at 30°.

It has been firmly established that these sugar solutions warm when diluted adiabatically. If we were then to accept the suggestion made by Woods that negative heats of dilution imply an association of solute molecules, the amount of which becomes greater at the higher temperatures, then the dynamical explanation would be that the increased association more than balanced the increase of kinetic pressure due to the rise in temperature.

Callender<sup>8</sup> has elaborated the vapor-pressure theory of Poynting and according to his view, when the heat of dilution is small, as it is, at any rate, with moderately strong solutions,

$$\Pi_r = \frac{N-an}{N-an+n} \pi_0$$

where *a* is a hydration factor representing the number of solvent molecules associated with each molecule of solute;  $\Pi_r$ , the vapor pressure of the solution;  $\Pi_0$ , the vapor pressure of the solvent; *N*, the mol fraction of the solvent; *n*, the mol fraction of the solute. If, on the other hand, Callender's hydration factor *a* changes, owing to the formation of simpler hydrates at the higher temperature, then one might consider the increase in effective dilution due to the liberation of the water previously attached to the sugar molecules to be responsible for the decrease in the osmotic pressure.

Woods also integrates the equations of Porter as applied to the results of Berkeley and Hartley

$$P = \frac{nRT}{V-nb}$$

and obtains 
$$\frac{dP}{dT} = \frac{P}{T} \left( 1 + \frac{P}{R} \frac{db}{dT} \right)$$

which makes *P* independent of the temperature when  $db/dT = -R/P$ . Then, for a solution whose osmotic pressure is 180 atmospheres, a loss of 1 molecule of water for each 40° rise of temperature would suffice in order that the osmotic pressure remain unchanged with rise in tem-

<sup>8</sup> Callender, *Proc. Roy. Soc.*, 80A, 466 (1908).

perature. A greater rate of dehydration than this would involve a decrease of the osmotic pressure with rise of temperature.

Woods, however, believes that this stage is not reached in the cases he studied and attributes the apparent decrease in his calculated values to a too rapid variation of the ratio of  $\Pi_0/\Pi_\infty$  with temperature. This conclusion seems unjustified. The loss by dehydration must reach such a magnitude at concentrations of 6 *M* and over that the increase in solvent due thereto more than balances the increase of kinetic pressure due to rise in temperatures.

### Summary.

1. In this article the authors describe a modification of the method used by Frazer and Myrick for measuring the osmotic pressure. The principle feature of the new apparatus is the use of the water interferometer in determining the magnitude of the pressures developed.

2. The apparatus affords a decided improvement over the method of Frazer and Myrick, being somewhat quicker in action and more dependable. Pressures up to 273 atmospheres have been measured, while the pressure chambers have been calibrated up to 330 atmospheres.

3. Measurements over the entire range of solubility are given for 30° and 55.7°.

4. Attention is called to the results of Woods as calculated for vapor-pressure measurements, and it is shown that his results, showing a decrease in osmotic pressure with rise in temperature with concentrated solutions, are relatively correct although his actual values for the osmotic pressure seem to be high as compared with these direct measurements.

BALTIMORE, MARYLAND.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. I, 7.]

## THE EQUILIBRIUM IN MIXTURES OF BINARY ELECTROLYTES.

By CHARLES A. KRAUS.

Received August 24, 1921.

### 1. Introduction.

The determination of the equilibrium in a mixture of electrolytes is a problem of considerable practical importance since many of the reactions with which we have to deal are carried out in mixtures of this kind. If the law of mass action is applicable to the resulting equilibrium, then the problem is in general soluble, provided intermediate ions are not formed. In all likelihood this condition is fulfilled in mixtures of binary electrolytes, but, as Harkins<sup>1</sup> has pointed out, when higher types of salts are present, intermediate ions are probably formed. The following discussion will therefore be limited to mixtures of binary electrolytes.

<sup>1</sup> Harkins, *THIS JOURNAL*, 33, 1807 (1911); 38, 2679 (1916).

In mixtures of strong electrolytes the problem of determining the concentration of the various molecular species present is complicated owing to the fact that the law of mass action in its simple form does not hold. We therefore have no means for calculating the equilibrium in these mixtures save such as are purely empirical in character. In the past the determination of the equilibrium in mixtures of strong electrolytes has been founded upon the isohydric principle of Arrhenius.<sup>2</sup> This principle has a theoretical foundation so long as the electrolytes involved in the reaction obey the simple law of mass action, but in the case of strong electrolytes this relation is purely an empirical one.

Presumably, in a mixture of strong electrolytes where the mass-action law does not hold, the various molecular species present will obey laws similar to those obeyed by the same molecular species in solutions containing a single electrolyte. The form of the function assumed as governing the equilibrium in a mixture should therefore agree with that of the salts alone in aqueous solution. Assuming that the ionization is measured by the ratio  $\Lambda/\Lambda_0$ , the form of the function in the case of pure electrolytes is known, although the equation remains uncertain. Nevertheless, various empirical functions which have been proposed account for the experimental values in the case of binary electrolytes with considerable precision over large ranges of concentration. As we shall see presently, the isohydric principle, when formulated mathematically, reduced to the proper form in the case of a solution of a single binary electrolyte. It is interesting to determine what other functions may be assumed to hold in mixtures which will reduce to the same form in the case of a solution of a single electrolyte.

## 2. The Isohydric Principle.

The isohydric principle is based upon the observation that if two electrolytes, having an ion in common, are mixed, then the ionization of the two electrolytes in the mixture will be the same as that in the original solutions before mixing, if the concentrations of the common ion in these solutions before mixing are equal. This result is a consequence of the law of mass action. Let  $M_1^+$  and  $X^-$  be the concentration of the ions in two solutions, where  $X^-$  is that of the common ion. If the concentrations of the common ion in the two solutions are the same before mixing, then obviously we have

$$M_1^+ = M_2^+ = X^-. \quad (1)$$

The total salt concentrations of the two solutions  $C_1$  and  $C_2$  will in general be different. Let  $V_1$  liters of the first solution be mixed with  $V_2$  liters of the second solution. If the conditions of Equation 1 are fulfilled, and if no displacement takes place in the equilibrium on mixing, then we should

<sup>2</sup> Arrhenius, *Z. physik. Chem.*, 5, 1 (1890); compare also 2, 284 (1888).

have for the concentration of the ions  $M_1^+$  in mixture the value  $\frac{M_1 + V_1}{V_1 + V_2}$  for that of the common ion  $\frac{M_1 + V_1 + M_2 + V_2}{V_1 + V_2}$ , and for that of the unionized fraction of the first salt  $M_1X_1 \left( \frac{V_1}{V_1 + V_2} \right)$ .

If the law of mass action holds, we have,

$$\frac{M_1 + V_1}{V_1 + V_2} \times \frac{M_1 + V_1 + M_2 + V_2}{V_1 + V_2} \times \frac{V_1}{M_1X_1(V_1 + V_2)} = K_1. \quad (2)$$

Equation 1 being fulfilled, it is obvious that we have

$$\frac{M_1 + V_1 + M_2 + V_2}{V_1 + V_2} = M_1^+;$$

and Equation 2 reduces to

$$\frac{M_1^+ + X_1^-}{M_1X_1} = K_1.$$

In other words, if the conditions expressed in Equation 1 is fulfilled by the original solutions before mixing, then no displacement takes place in the equilibrium when these solutions are mixed in any proportions what ever.

In the case of mixtures of weak acids and bases where the law of mass action holds, this consequence of the law of mass action has been substantiated. Since the conductance of solutions of acids is due chiefly to the hydrogen ion, it follows that the conductance of a mixture of two acids will be the same as that of the acids before mixing, provided the original solutions have the same specific conductance. In this it is assumed that the conductance of the anion in the two acids is the same. If this condition is not fulfilled, it is obvious that the conductance of the mixture will vary as a linear function of the composition of the two solutions which have the same concentration of the hydrogen ion.

It has been found, however, that even in the case of solutions which do not conform to the law of mass action, that is, solutions of strong electrolytes, a similar condition holds. If, for example, solutions of ammonium chloride and potassium chloride are mixed, the specific conductance of the mixture will be (approximately) independent of the proportions of the original solutions taken, provided that these solutions have the same specific conductance. Apparently, then, the isohydric principle holds even though the law of mass action is not obeyed. This principle has, therefore, been employed for the purpose of calculating the equilibrium in mixtures of strong electrolytes.

The law of equilibrium for a given electrolyte in a mixture must obviously reduce in the limit to that of solutions of electrolytes in the pure solvent. It has been shown that for strong electrolytes the following equation<sup>3</sup> holds approximately,

$$P_i/C_u = D(\Sigma C_i)^m + K, \quad (3)$$

where  $P_i$  is the value of the ion product,  $C_u$  is the concentration of the unionized fraction,  $\Sigma C_i$  is the concentration of all the positive or negative ions in the solution, and  $D$ ,  $m$  and  $K$  are constants. It is evident that this equation conforms to the isohydric principle. Indeed, any equation of the form

$$P_i/C_u = F(\Sigma C_i) \quad (4)$$

conforms to the isohydric principle. Here  $F(\Sigma C_i)$  is any explicit function of the total ion concentration of the mixture. For, on mixing two solutions whose ion concentrations are  $C_i'$  and  $C_i''$ , the equilibrium will be unaffected by the relative volumes of the solutions mixed, provided that  $C_i' = C_i''$ . Equation 4, therefore, is the analytical expression for the equilibrium in the mixture according to the isohydric principle. In the limit, as the second component in the mixture disappears, the equation reduces to that of the first salt alone. Obviously the same equation may be applied to mixtures of electrolytes without a common ion.

### 3. An Alternative Principle Which May Be Assumed to Govern the Equilibrium in Mixtures of Electrolytes.

Equation 4 is not the only function which fulfils the condition that it reduces to the form of Equation 3 in the case of a single electrolyte. We may assume for the mixture the function,

$$P_i/C_u = F(P_i), \quad (5)$$

where  $P_i$  is the ion product. In the limit the concentrations of the positive and negative ions become equal for a solution of a single electrolyte and consequently the equation reduces to the form of Equation 3. Equations 4 and 5, therefore, both fulfil the condition that they reduce to the proper form in the special case that only a single electrolyte is present in solution. In order to determine which of these equations is more nearly applicable to a mixture, it is obviously necessary to measure some independent property of these mixtures; such as the conductance, for example. Assuming that the conductance of the ions in the mixture is the same as that of the same ions dissolved alone in water, it is possible to calculate the specific conductance of the mixture if the form of the conduction functions for the pure electrolytes is known and if a function is assumed to hold for the mixture. If the assumed function is correct, then the calculated specific conductance of the mixture should correspond

<sup>3</sup> Kraus and Bray, *THIS JOURNAL*, 35, 1315 (1913); Kraus, *ibid.*, 42, 1 (1920).

to the measured specific conductance within the limits of experimental error. If the calculated values do not so correspond, it indicates that the function so assumed for the mixture is not applicable.

#### 4. Test of Functions 4 and 5 in the Case of Mixtures of Sodium Chloride and Hydrochloric Acid.

Bray and Hunt<sup>4</sup> have measured the specific conductance of mixtures of sodium chloride and hydrochloric acid in water at 25°. They have likewise calculated the specific conductance of the mixtures assuming the isohydric principle; that is, assuming Equation 4. The results are given in the following table, where the concentrations of sodium chloride and

TABLE I.

MEASURED SPECIFIC CONDUCTANCE OF MIXTURES OF SODIUM CHLORIDE AND HYDROCHLORIC ACID COMPARED WITH VALUES CALCULATED ACCORDING TO EQUATIONS 4 AND 5.

No.	Concentration (approx.) Millimols.		Measured.	Specific Conductance <i>L.</i>			
	NaCl.	HCl.		Calc. Eq. 4.	Diff. %.	Calc. Eq. 5.	Diff. %.
1	100	100	47.25	48.21	-2.1	47.09	+0.3
2	100	50	29.14	29.62	-1.6	28.82	+1.1
3	100	20	18.06	18.31	-1.4	17.84	+1.2
4	100	10	14.36	14.50	-1.0	14.18	+1.2
5	100	5	12.52	12.59	-0.6	12.39	+1.1
6	100	2	11.41	11.45	-0.3	11.35	+0.5
Mean.				—	-1.15		+0.85
7	20	50	21.75	21.89	-0.7	21.65	+0.4
8	20	20	10.157	10.27	-1.1	10.13	+0.3
9	20	10	6.253	6.307	-0.9	6.221	+0.5
10	20	4	3.889	3.919	-0.8	3.870	+0.3
11	20	2	3.101	3.118	-0.6	3.094	+0.2
12	20	1	2.709	2.721	-0.4	2.702	+0.3
Mean.					-0.75		+0.33
13	5	12.5	5.651	5.678	-0.5	5.646	+0.1
14	5	5	2.632	2.650	-0.7	2.634	-0.1
15	5	2	1.621	1.630	-0.6	1.619	+0.1
16	5	1	1.011	1.016	-0.5	1.010	+0.1
Mean.					-0.57		+0.05

hydrochloric acid are given in the second and third columns respectively, the measured specific conductance in the fourth column, and in the fifth column the specific conductance calculated according to Equation 4. Finally, in the sixth column are given the percentage deviations between the measured and the calculated values. In the same table, in Column

<sup>4</sup> Bray and Hunt, *THIS JOURNAL*, 33, 781 (1911).

7, are given the values of the specific conductance calculated according to Equation 5, and in the last column the percentage deviations between the calculated and the observed values.

Comparing the measured values with those calculated on the basis of Equation 4, it is seen that the deviations from the isohydric principle are consistently larger than any conceivable experimental error. With mixtures containing 0.1 *N* solutions of sodium chloride, the mean error is -1.15%; for 0.02 *N* solutions of sodium chloride, the mean deviation is -0.75%; and for 0.005 *N* solutions of sodium chloride, the mean deviation is -0.57%. The values of the specific conductance calculated according to Equation 4 are throughout greater than the observed values. At the lower concentrations the agreement between the observed and calculated values is measurably better than at the higher concentrations, but, in all cases, the discrepancies are far in excess of any conceivable experimental error. It is true that at the high concentrations the results may be affected owing to the influence of viscosity, but this certainly cannot be the case at the lowest concentrations.

The values of the specific conductance as calculated according to Equation 5 exhibit, throughout, a better agreement with the measured values than those calculated according to the isohydric principle, particularly at the lower concentrations. In mixtures containing 0.10 *N* sodium chloride the mean deviation of +0.85% is unquestionably far in excess of the experimental error. However, in mixtures containing 0.02 *N* sodium chloride the mean deviation has fallen to +0.33%, which is not greatly in excess of the experimental error. Finally, in mixtures containing 0.005 *N* sodium chloride, the mean deviation has fallen to 0.05%, which is well within the limits of experimental error. At the higher concentrations, the values of the specific conductance, calculated according to Equation 5, are throughout somewhat less than the measured values. At the lowest concentration, namely, 0.005 *N* sodium chloride, the differences are both positive and negative.

In calculating the specific conductance of the mixtures according to Equation 5, the values assumed for  $\lambda_0$  were 127.0 and 424.0 for sodium chloride and hydrochloric acid, respectively. Bray and Hunt state that the calculated value of the specific conductance is not materially affected by the value assumed for  $\lambda_0$ . So, also, in calculating the specific conductance according to Equation 5, the values assumed for  $\lambda_0$  have only a secondary effect upon the resulting value of the specific conductance. For example, assuming for hydrochloric acid and sodium chloride the  $\lambda_0$  values 422 and 125.4 respectively, the calculated specific conductance according to Equation 5 is 3.097 for point 11. The divergence resulting from change in the values of  $\Delta_0$  naturally varies somewhat with the concentration.



The results given above cannot be said to establish the correctness of the principle expressed by Equation 5, in the case of mixtures of strong electrolytes. Nevertheless, it appears that this principle yields results which are more nearly in agreement with experiment than are those based on the isohydric principle, which is commonly employed for this purpose. The isohydric principle leads to erroneous results even at very low concentrations, whereas the alternative principle leads to results in agreement with the experimental values at low concentrations. It is, of course, possible that in the case of mixtures other than those of sodium chloride and hydrochloric acid a similar agreement may not be found. However, electrolytes of a given type in aqueous solutions exhibit such similarity in their behavior that it is probable that similar results will be found in other mixtures.

The isohydric principle has been extensively employed for calculating the concentrations of the various molecular constituents present in mixtures. Since this principle does not hold, it is obvious that the concentrations of the various constituents so found are subject to considerable error. These errors may not greatly affect the concentrations found for certain of the molecular species, but, in the case of others, the errors may be very great. In those cases where the effect of electrolytes upon the solubility of other electrolytes has been studied, the conclusion has been reached that the concentration of the un-ionized fraction of the salt present as solid phase is greatly diminished by the addition of a second electrolyte. Since the isohydric principle, which underlies these calculations, is not correct, it seems not improbable that the great change found in the concentration of the un-ionized fraction is a consequence of applying to the mixture a principle which in fact does not hold. If we make the assumption that the un-ionized fraction of a salt, which is present as solid phase, remains constant on the addition of a second electrolyte, then it follows, from Equation 5, that the ion product likewise remains constant. This result is, on the whole, in agreement with observations on the solubility of binary electrolytes in the presence of other electrolytes with a common ion. In another paper the solubility relations in the case of binary electrolytes will be discussed more in detail.

### Summary.

1. It is shown that the isohydric principle, when applied to mixtures of electrolytes, leads to a functional relation of the form  $(C_i)^2/C_{\pm} = F(2C_i)$ .
2. As the concentration of the second electrolyte diminishes, the function  $P_i/C_{\pm} = F(P_i)$  reduces, in the limit, to the same form as the function resulting from the isohydric principle.
3. The values of the specific conductance of mixtures of sodium chlo-

ride and hydrochloric acid as calculated according to this principle are shown to furnish a better agreement with the measured values than are those based on the isohydric principle.

WORCESTER, MASSACHUSETTS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 9.]

## GHOSH'S THEORY OF ELECTROLYTIC SOLUTIONS.

By CHARLES A. KRAUS.

Received September, 10, 1921.

### 1. Introduction.

The so-called "anomaly" of solutions of strong electrolytes has been one of the outstanding problems of chemistry almost since the inception of the Ionic Theory. Attempts which have been made to account for the behavior of these solutions from a theoretical standpoint have not met with marked success. In most instances such theories have been designed to account for only a limited number of the characteristic properties of electrolytic solutions and they have rarely been extended to include non-aqueous solutions.

In a series of articles<sup>1</sup> Ghosh has recently advanced a theory of electrolytic solutions which is very comprehensive in its scope, and which is founded upon somewhat novel assumptions with regard to the nature of electrolytes and their solutions. He has developed relations to account for nearly all important properties of electrolytic solutions in different solvents and has compared the consequences of his theory with existing experimental data. Therefrom he draws the conclusion that his theory is fully substantiated.

If Ghosh's theory is correct, it will be necessary to alter greatly the present day treatment of the properties of electrolytic solutions. Since, ultimately, the soundness of any theory must be judged by the degree of correspondence between the experimental data and the consequences resulting from the theory, a consideration of the postulates and assumptions upon which the theory of Ghosh is founded may be deferred until this theory has been examined from an experimental point of view.<sup>2</sup> The question to be answered is: To what degree of precision is Ghosh's theory able to account for the experimental data? If the theory is correct in its essential details, as Ghosh believes it to be, then it should render substantial account of the experimental results. Systematic deviations, between the consequences of the theory and the experimental facts should

<sup>1</sup> Ghosh, *J. Chem. Soc.*, 113, 449, 627, 777, 790 (1918).

<sup>2</sup> Partington (*Trans. Faraday Soc.*, 15, 111 (1919-20)) has criticized certain features of Ghosh's theory and Ghosh has replied to the same (*ibid.*, 15, 154 (1919-20)). This discussion, however, has left many points in an uncertain state.

appear only under conditions not included within the scope of the theory as postulated.

## 2. Method of Testing the Equation.

In examining a theory of this kind, whose purpose is to account for the relation between a dependent and a number of independent variables, it is practically necessary to resort to graphical methods, for in no other way is it possible to comprehend at a glance the degree of correspondence between theory and experiment, as one or another of the independent variables is subjected to change. The only graph which has a decided value for this purpose is one which leads to a linear relation between the independent and the dependent variables under consideration. Where the equations involving the variables in question are complex, other variables must be chosen such that a linear relation exists between them, which, in some cases, renders the problem difficult, since various undetermined constants may be involved. In the case of the Ghosh Equation, however, a comparison by graphical method is both simple and conclusive, since a linear relation exists between the experimentally determined variables themselves. The conductance is expressed as a function of the concentration by means of the equation

$$\log \Lambda = \log \Lambda_0 - \frac{\beta C^{1/3}}{DT} \quad (1)$$

where

$$\beta = \frac{NE^2 (2N)^{1/3}}{2.3026 mR}$$

Here  $N$  is Avogadro's number,  $6.16 \times 10^{23}$ ,  $E$  is the electrostatic unit of charge,  $4.7 \times 10^{-10}$  e.s.u.,  $R$  is the value of the gas constant in absolute units, and  $m$  is a factor depending upon the number of ions  $n$  produced from a single neutral molecule and upon the number of charges associated with a single ion, as well as the manner of distribution of these ions in the solvent medium. It is evident that, for a given solvent at a given temperature, the logarithm of the equivalent conductance is a linear function of the cube root of the concentration. Any systematic deviations between the experimental and the theoretical values will at once be apparent if the experimental values of  $\log \Lambda$  and of  $C^{1/3}$  are represented graphically. This method of treatment, moreover, obviates any assumption with respect to the values for the constants  $\Lambda_0$  and  $\beta$ , since, if the theoretical equation holds, the experimental values will follow a linear relation from which the values of the constants may be uniquely determined.

## 3. Aqueous Solutions of Potassium Chloride.

In Fig. 1, values of  $\log \Lambda$  are plotted as ordinates and those of  $C^{1/3}$  as abscissas for solutions of potassium chloride in water at  $18^\circ$ ; the data

being due to Kohlrausch and Maltby,<sup>3</sup> and to Washburn and Weiland.<sup>4</sup> According to Ghosh,  $\beta$  should have the value  $3.620 \times 10^3$  for binary electrolytes in water,  $C$  being expressed in mols per liter. In the figure the straight line drawn, passing through the point  $C^{1/2} = 0.2154$ , corresponds to Ghosh's equation. Ghosh assumes a value of 122.5 for the conductance of potassium chloride at 0.01  $N$ , in determining the value of  $\Lambda_0$ . The value due to Kohlrausch, however, is 122.37. For the purpose of comparison, therefore, the straight line corresponding to Ghosh's equation has been drawn through this point at an angle corresponding to the value of  $\beta$  assumed by Ghosh, namely,  $\beta = 3.620 \times 10^3$ .

In the following table are given the calculated and observed values of  $\Lambda$  for solutions of potassium chloride in water at 18°, together with the differences between the observed and the calculated values.

TABLE I.

COMPARISON OF OBSERVED AND CALCULATED VALUES OF  $\Lambda$  FOR POTASSIUM CHLORIDE IN WATER AT 18°.

	$\Lambda_0 = 132.06.$		$\beta = 3.620 \times 10^3.$		$T = 291.$	$D = 81.$	
$V$ .....	$5 \times 10^4$	$2 \times 10^4$	$10^4$	$5 \times 10^3$	$2 \times 10^3$	$10^3$	$5 \times 10^2$
$\Lambda_{\text{calc}}$ .....	130.80	130.35	129.90	129.35	128.40	127.47	126.30
$\Lambda_{\text{obs}}$ .....	129.51	129.32	129.00	128.70	128.04	127.27	126.24
$\Lambda_{\text{obs.}} - \Lambda_{\text{calc.}}$ ...	-1.39	-1.03	-0.90	-0.45	-0.36	-0.20	-0.06
$V$ .....	$2 \times 10^2$	$10^2$	50	20	10	5	2
$\Lambda_{\text{calc}}$ .....	124.31	122.37	119.97	116.9	112.1	107.4	99.7
$\Lambda_{\text{obs}}$ .....	126.24	122.37	119.90	115.6	111.8	107.5	101.3
$\Lambda_{\text{obs.}} - \Lambda_{\text{calc.}}$ ...	+0.03	$\pm 0.00$	-0.07	-0.3	-0.3	-0.1	+1.6

The conductance values, as determined by Kohlrausch and by Washburn and Weiland have a relative precision greater than 0.1%. In all likelihood the mean error does not exceed 0.05%. At the higher concentrations the conductance is measurably affected by the viscosity change of the solution due to the added salt. Since Ghosh subsequently employs conductance values corrected for viscosity,<sup>5</sup> these corrected values have been employed in the comparison whose results are given above. It is evident that the observed values of  $\Lambda$  diverge from the theoretical curve at concentrations above approximately  $2 \times 10^{-2} N$  and below  $10^{-3} N$ . These deviations greatly exceed the probable experimental error. The experimental curve is concave toward the axis of concentrations in dilute solutions and convex toward this axis in concentrated solutions with an inflection point at an intermediate concentration. The curve resulting from Ghosh's equation is very nearly tangent to the experimental curve in the neighborhood of the inflection point. Whether

<sup>3</sup> Kohlrausch and Maltby, *Wiss. Abh. phys.-tech. Reichsanstalt*, 3, 210 (1900). Noyes and Falk, *THIS JOURNAL*, 34, 454 (1912).

<sup>4</sup> Washburn and Weiland, *ibid.*, 40, 137 (1918).

<sup>5</sup> Ghosh, *Trans. Faraday Soc.*, 15, 154 (1919-20).

this coincidence possesses a real significance or is merely an accidental result may be determined by an examination of non-aqueous solutions. It is well known that at lower concentrations the ionization curves for aqueous solutions of different binary electrolytes are practically identical and consequently what is true of solutions of potassium chloride will be true of other solutions of binary salts in water.

Ghosh's equation reduces to the form  $\Lambda_0 - \Lambda = AC^{1/2}$ , at very low concentrations. This equation is one of the empirical functions employed by Kohlrausch for representing the equivalent conductance of electrolytes as a function of their concentration. Ghosh looks upon this as lending support to his theory. It may be noted, however, that, as Kohlrausch himself pointed out, the cube root function yields a curve concave toward the axis of concentrations at low concentrations.<sup>6</sup> In determining the value of  $\Lambda_0$ , therefore, Kohlrausch employed a corre-

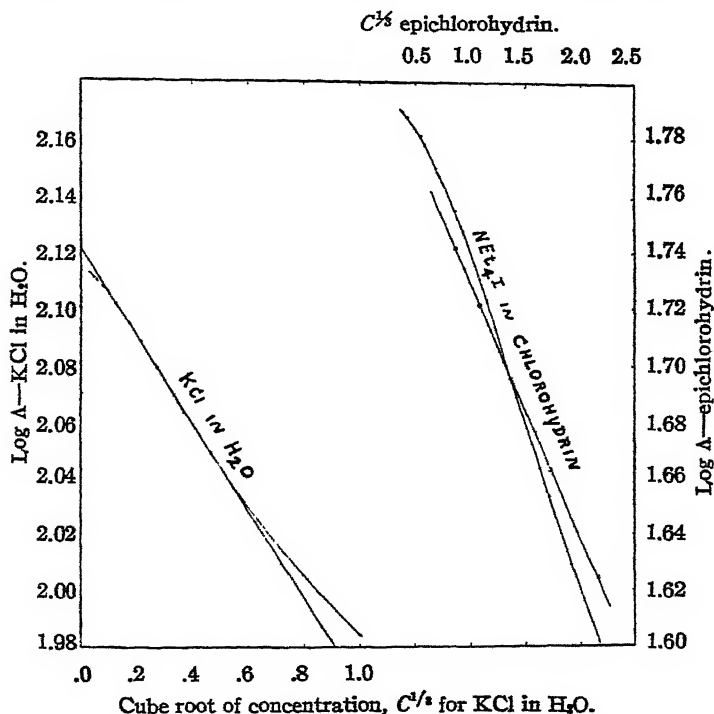


Fig. 1.—Curves for KCl in  $H_2O$  and  $NEt_4I$  in epichlorohydrin.

sponding extrapolation function in which the concentration appears with the exponent  $1/2$  in place of  $1/3$ . This result of Kohlrausch is in entire accord with the results as plotted in Fig. 1, where the experimental curve is markedly concave toward the axis of concentrations at low concen-

<sup>6</sup> Kohlrausch and Maltby, Ref. 3., p. 218.

trations. It is clear that the equation of Ghosh cannot be looked upon as exact. However, in view of the fact that the theoretical curve coincides in slope with the experimental curve in the neighborhood of the inflection point, it will be necessary to examine solutions in other solvents than water in order to determine whether or not Ghosh's theory contains in it certain elements of truth.

#### 4. Application to Freezing-Point Data.

Before proceeding to a consideration of the conductance curve in non-aqueous solutions, we may examine the results of Ghosh's theory as applied to the freezing points of aqueous solutions of electrolytes. For the value of the van't Hoff factor  $i$ , Ghosh obtains the equation<sup>7</sup>

$$i = n \left( 1 - \frac{1}{3} \log \frac{1}{\gamma} \right), \quad (2)$$

where  $n$  is the number of ions into which the electrolyte dissociates, and  $\gamma$  is the ionization, as calculated from Ghosh's Equation 1. According to the usual ionic theory, the value of  $i$  is given by the equation,  $i = 1 + (n-1)\gamma$ , where, as before,  $n$  is the number of ions into which the electrolyte dissociates and  $\gamma$  is the degree of ionization as calculated from conductance measurements, the value of  $\Lambda_0$  being extrapolated by means of empirical functions.

It is a well-known fact that for dilute solutions of many electrolytes, such as potassium chloride, for example, the value of  $i$ , as determined from freezing-point measurements, agrees within the limit of experimental error with the value as determined from conductance measurements on the basis of the usual ionic theory. It follows, therefore, that the values of  $i$ , as calculated from Equation 2, cannot be in agreement with the experimentally determined values of  $i$ . In the following tables are given the values of  $i$  as calculated according to the equations of Ghosh, assuming the constants given in Table I, together with the experimentally determined values of Adams<sup>8</sup> and the values calculated from conductance measurements in the usual way.

TABLE II.

COMPARISON OF THE EXPERIMENTALLY DETERMINED VALUES OF  $i$  WITH THOSE CALCULATED ACCORDING TO GHOSH'S EQUATION AND THOSE CALCULATED ACCORDING TO THE IONIC THEORY.

$C \times 10^3$	2.	5.	10.	20.	50.	100.
$i_{\text{Ghosh}}$ .....	1.970	1.960	1.949	1.936	1.913	1.891
$i_{\text{Adams}}$ .....	1.969	1.961	1.943	1.922	1.888	1.861
$i_{\text{cond.}}$ .....	1.971	1.956	1.941	1.918	1.889	1.860

From the table it is evident that, at concentrations above 0.01  $N$ , the values as calculated from Ghosh's equation deviate systematically

<sup>7</sup> Ghosh, Ref. 5, p. 707.

<sup>8</sup> Adams, THIS JOURNAL, 37, 481 (1915).

from the determined values by amounts which are in excess of the experimental error. These deviations exceed 1% at 0.1 *N*. Another fact which argues strongly against the adequacy of Ghosh's equation is the fact that the values of  $i$  as determined from freezing-point measurements differ for different electrolytes at higher concentrations. Since the value of  $i$  as calculated from Ghosh's equation is the same for all electrolytes of the same type, it follows that the observed variation in the experimentally determined values of  $i$  are not accounted for by his theory. In the following table are given values of  $i$  for a number of binary electrolytes at a concentration of 0.1 *N*.

TABLE III.

VALUES OF  $i$  AT 0.1 *N* CONCENTRATION FOR DIFFERENT ELECTROLYTES IN WATER.

Salt.	KCl.	KNO <sub>3</sub> .	KIO <sub>3</sub> .	NaIO <sub>3</sub> .	LiCl.	KOH.	HCl.
$i$ .....	1.861	1.787	1.764	1.772	1.901	1.865	1.917

The values of  $i$  for the first four electrolytes are derived from the very exact determinations of Adams<sup>8</sup> and of Hall and Harkins,<sup>9</sup> while the remaining values are taken from the tables given by Noyes and Falk.<sup>10</sup> It is seen from this table that the extreme variation in the value of  $i$  is from 1.764 to 1.917. This variation in the value of  $i$  for different electrolytes at higher concentration cannot be ascribed to experimental error. It represents, in fact, a real difference in the properties of the solutions of these substances. Ghosh's theory, being founded upon the assumption that all electrolytes are completely ionized, is obviously unable to account for the divergence in the properties of different electrolytes of the same type. In the case of aqueous solutions, as has already been pointed out, the ionization curves for different electrolytes do not differ very greatly, but it is evident that the freezing-point curves differ to a much greater extent. We shall see that, in non-aqueous solvents, solutions of electrolytes of the same type differ very largely as regards their ionization values according to the conductance method also.

### 5. Non-Aqueous Solutions.

The most extensive material for testing the applicability of Ghosh's theory is found in conductance data relating to solutions in non-aqueous solvents. That Ghosh experienced some difficulty in attempting to apply his equations to solutions in non-aqueous solvents is evidenced by the fact that he was forced to assume more or less arbitrary types of ionization for solutions of simple binary salts. In the case of solutions of tetraethyl-ammonium iodide, for example, he assumes a ternary ionization of the type  $(MX)_2 = M_2^{++} + 2X^-$ . No independent evidence exists in support of this assumption. As we shall see below, this assumption

<sup>8</sup> Hall and Harkins, THIS JOURNAL, 38, 2658 (1916).

<sup>10</sup> Noyes and Falk, *ibid.*, 32, 1011 (1910).

does not suffice to account for the extremely varied behavior of solutions in non-aqueous solvents. Indeed, to one familiar with the properties of solutions in such solvents, it is at once evident that the theory will meet with great difficulties, for, according to Ghosh's Equation, the ionization in a given solvent at a given temperature is independent of the nature of the electrolyte, while the experimental data indicate that different electrolytes of the same type, even at low concentrations, exhibit a varying degree of ionization depending upon the nature of the electrolyte, as well as upon that of the solvent.

Below are considered solutions of typical salts in a few non-aqueous solvents. The number of examples might be greatly multiplied, but those which are presented suffice to bring out clearly the inadequacy of Ghosh's theory. The solutions chosen are those for which experimental data of a relatively high degree of precision are available down to comparatively low concentrations. In Fig. 1 is shown the curve for solutions of tetra-ethyl-ammonium iodide in epichlorohydrin.<sup>11</sup> The experimental curve is manifestly similar to that of potassium chloride in water. The characteristic deviations from Ghosh's equation, however, are more accentuated. Ghosh's calculated values, assuming a ternary ionization process, are represented on the figure by circles, a straight line having been drawn through them. Had a binary ionization process been assumed, the straight line corresponding to his equation would have been inclined much less steeply than the one drawn. It is evident that the deviations between the experimental and the theoretical curves are far in excess of any possible experimental error. A somewhat better agreement between the calculated and observed values at intermediate concentrations would be obtained by drawing a straight line tangent to the experimental curve in the neighborhood of the inflection point at approximately  $10^{-3} N$ . This line would be inclined more steeply than that due to Ghosh and would consequently correspond to a value of  $\beta$  greater than  $6.808 \times 10^3$ , which is that derived by Ghosh for a ternary ionization. But even in this case, at concentrations below  $10^{-3} N$ , the deviations between the observed and the calculated values would be far in excess of the experimental error. From the general form of the curve, also, it is evident that at higher concentrations the deviations would ultimately become marked. In the case of these solutions, however, experimental data are not available at higher concentrations. The value of  $\beta$  corresponding most nearly with the experimental curve is  $9.38 \times 10^3$ .

In Fig. 2 are plotted the results for solutions of potassium iodide in liquid ammonia according to the measurements of Franklin<sup>12</sup> and for tetra-propyl-ammonium iodide in ethylene chloride according to measure-

<sup>11</sup> Walden, *Z. physik. Chem.*, 54, 212 (1905).

<sup>12</sup> Franklin, *ibid.*, 69, 290 (1909).



ments of Walden.<sup>13</sup> Considering first solutions of potassium iodide in liquid ammonia, the discrepancy between Ghosh's theory and the experimental values is obvious. Down to concentrations as low as 0.001 *N*, the curve is distinctly convex toward the axis of concentrations. At somewhat higher concentration this convexity is extremely marked. This type of curve is characteristic of solutions in solvents of relatively low dielectric constant; that is, in the neighborhood of 20. In such solvents, at concentrations above 0.01 *N*, the equivalent conductance, in general, changes only very little with increasing concentrations; and, indeed, in certain cases increases with increasing concentration. At very

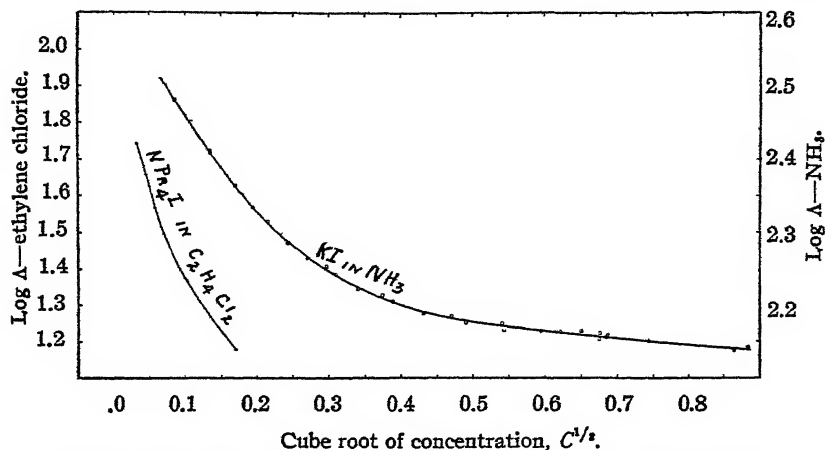


Fig. 2.—Plot of Ghosh's equation for KI in  $\text{NH}_3$  and  $\text{NPr}_4\text{I}$  in  $\text{C}_2\text{H}_4\text{Cl}_2$ .

low concentrations conductance measurements are not available in the case of potassium iodide in ammonia, but from the known similarity in the behavior of solutions of different electrolytes in ammonia at low concentration it is clear that, at concentrations slightly below 0.001 *N*, the experimental curve would be concave toward the axis of concentrations. This is clearly brought out in the case of potassium nitrate in ammonia, which is shown in Fig. 3.

The curve for tetra-propyl-ammonium iodide in ethylene chloride is much steeper than that of potassium iodide in ammonia. At the higher concentrations the curve is again convex toward the axis of concentrations, while at the lowest concentrations the curve is slightly concave toward this axis. The best straight line which could be drawn through the points of this curve would lie tangent to the curve in the neighborhood of the inflection point, passing through a point at about 0.001 *N*. This yields for  $\beta$  the value  $20.78 \times 10^3$ . It is clear, however, that the equation of Ghosh can reproduce the experimental results within the limits of error

<sup>13</sup> Walden, *Z. physik. Chem.*, **78**, 276 (1911).

only over an extremely small concentration interval in the neighborhood of the point through which the theoretical curve is arbitrarily made to pass.

According to Ghosh's theory, the ionization of electrolytes in a given solvent has the same value for all electrolytes of the same type under given conditions of temperature, pressure and concentration. It is known that the conductance curves of different binary electrolytes in liquid ammonia exhibit a great variety of form, even at comparatively low concentrations. For example, many of these curves intersect one another. This is not in harmony with Ghosh's theory in its present form. In Fig. 3 are shown the curves for potassium nitrate and silver iodide in liquid ammonia at its boiling point, the experimental values being due to Frank-

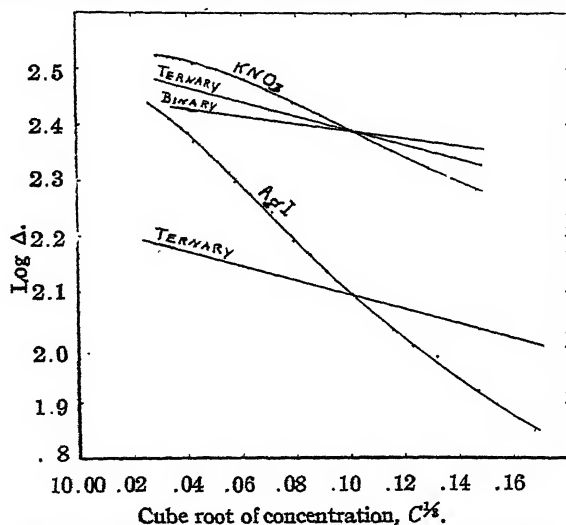


Fig. 3.—Plot of Ghosh's equation for solutions in  $\text{NH}_3$ .

lin and Kraus.<sup>14</sup> Considering first the curve for potassium nitrate, it is seen that at concentrations a little below 0.001  $N$  the curve is distinctly concave toward the axis of concentrations, while above this point the curve is convex toward this axis, having an inflection point in the neighborhood of 0.001  $N$ . Intersecting the curve for potassium nitrate are drawn two straight lines representing Ghosh's Equation for a binary and a ternary assumed ionization process. These curves correspond to the values  $\beta = 3.620 \times 10^8$  and  $6.808 \times 10^8$  respectively. A straight line drawn through the experimental curve, passing through the maximum number of points in the neighborhood of the inflection point, corresponds to a value  $\beta = 12.63 \times 10^8$ . The curve for silver iodide shown on the same figure exhibits a smaller curvature than does that of potassium nitrate, both at low and high concentrations. If a straight line is drawn in such

<sup>14</sup> Franklin and Kraus, *Am. Chem. J.*, 23, 277 (1900).

manner as to pass through the maximum number of experimental points, it is necessary to assume a value of  $\beta = 25.44 \times 10^3$ , in place of  $6.808 \times 10^3$ . A straight line corresponding to a ternary ionization is shown on the figure.

In order to account for the varied inclination of the curves for different electrolytes in ammonia solutions, according to Ghosh's theory, it would be necessary to assume a large variety of ionization processes, or of the relative distribution of the charges in the medium. The values following from a ternary ionization do not account for any of the results obtained with solutions in liquid ammonia. Here, in contrast to aqueous solutions, the individual characteristics of the electrolyte come clearly into view. According to Ghosh's theory, we should expect the conductance curves to fall into a few distinct classes. This, however, is not the case. It follows, therefore, that the agreement which Ghosh believes to have existed in the case of non-aqueous solutions is not substantiated, and that, in fact, assuming binary and ternary ionization processes, his theory does not account for the experimental results in such solutions even approximately.

## 6. The Temperature Effect.

Ghosh believes that his theory accounts for the effect of temperature on the ionization of electrolytes. In order to determine the correctness of this conclusion the conductance of solutions of potassium iodide in sulfur dioxide at  $-33^\circ$  and at  $+10^\circ$  have been examined, the results of Franklin<sup>15</sup> being employed for this purpose. The curves for these solutions are shown in Fig. 4. It will be observed that even at concentrations as low as 0.001 *N* the curves are markedly convex toward the axis of concentrations. As the concentration increases, the convexity of the curves increases markedly and, at the higher temperature, the curve exhibits a minimum, corresponding to the minimum in the conductance-concentration curve of these solutions. It is well known that this phenomenon is a general one which reappears in the case of all solutions in solvents having a dielectric constant lower than approximately 16. The lower the dielectric constant, the lower is, in general, the concentration at which the minimum point occurs; and, in solvents of very low dielectric constant, this minimum point lies as low as 0.01 *N* or lower. It is clear that, in the case of solutions of this type, Ghosh's theory does not apply even approximately.

The two straight lines, drawn through the points on the curve corresponding to a concentration of 0.001 *N*, represent Ghosh's equation for a ternary ionization process. The values of the constant  $\beta$  have been calculated from the dielectric constant of the solvent at the temperatures

<sup>15</sup> Franklin, *J. phys. Chem.*, 15, 675 (1911).

in question. The values of the dielectric constant were determined by extrapolation from the measurements of Eversheim.<sup>18</sup> These were found to be 15.1 at  $+10^\circ$  and 19.0 at  $-33^\circ$ . It is evident that, according to Ghosh's theory, the temperature can have only a small influence upon the ionization of an electrolyte in sulfur dioxide, since the value of  $\beta/DT$  at  $+10^\circ$  is 1.592; and at  $-33^\circ$ , 1.492. The two conductance curves, therefore, should be very nearly parallel, according to Ghosh. As indicated in the figure, however, this is not the case; moreover, the in-

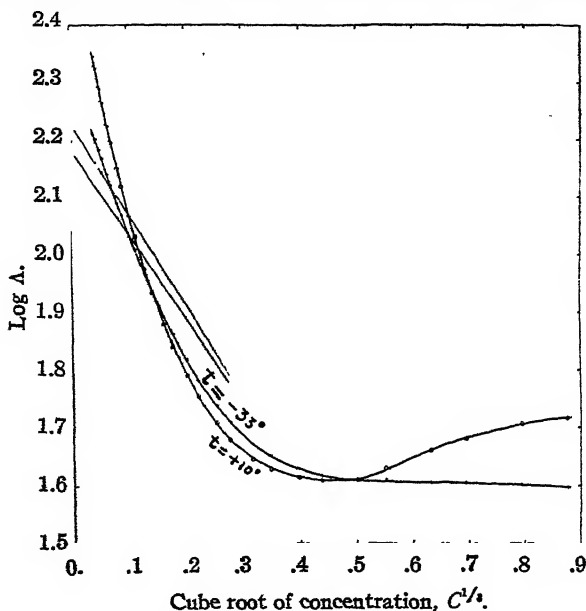


Fig. 4.—Plot of Ghosh's equation for KI in  $\text{SO}_2$  at  $-33^\circ$  and  $+10^\circ$ .

clination of the two curves in the neighborhood of  $0.001 N$  differs much more than corresponds to the change in the value of  $\beta/DT$ . If straight lines are passed through the points in the neighborhood of  $0.001 N$ , they yield the values  $\beta = 13.63 \times 10^3$  at  $-33^\circ$  and  $19.44 \times 10^3$  at  $+10^\circ$ , while, according to Ghosh, the value of  $\beta$  should be constant and equal to  $6.808 \times 10^3$ . Assuming that Ghosh's theory yields a rough approximation to the actual facts, it is obviously necessary to assume that  $\beta$  is not a constant independent of the temperature but, on the contrary, one whose value depends on the temperature. This has an important bearing on the interpretation of Ghosh's theory.

#### 7. The Variation of the Constant $\beta$ .

According to the theory of Ghosh, the ionization curves for different

<sup>18</sup> Eversheim, *Ann. Physik*, [4] 8, 539 (1902).

electrolytes in a given solvent at a given temperature should fall into a small number of types, depending upon the number of charges associated with an ion and upon their relative distribution in the solvent medium. Since, according to this theory, the conductance curves should consist of a system of parallel straight lines for a given value of  $\beta$ , assuming the temperature to remain constant, it follows that, in the plots, the conductance curves should approximate a series of parallel straight lines. An examination of the curves for different electrolytes in liquid ammonia solution shows that this is not the case. Furthermore, it follows from the conductance curves of solutions of potassium iodide in sulfur dioxide at different temperatures that  $\beta$  is not a constant for a given electrolyte, but is a function of the temperature. Since, therefore, for a given electrolyte, there is a continuous shift in the value of  $\beta$ , with temperature change, it is necessary to assume a continuous displacement in the ionization process and in the nature of the assumed fixed spatial relations of the ions in the medium. But it is also clear that, for a given electrolyte at a given temperature in a given solvent, the curve is not linear, as required by Ghosh's theory. It follows, therefore, that  $\beta$  is a function both of temperature and of concentration.

The conductance of aqueous solutions of potassium chloride has been measured with a high degree of precision to concentrations as low as  $2 \times 10^{-5} N$ . The commonly assumed value of 130.0 for the limiting conductance of potassium chloride solutions can scarcely be in error by more than a few tenths of a unit. Assuming, therefore, this value of  $\Delta_0$ , we may calculate the value of  $\beta$  for these solutions at different concentrations. The change in the value of  $\beta$  will, of course, be affected by the value chosen for  $\Delta_0$ , but it is to be borne in mind that a variation must necessarily result in the calculated value of  $\beta$  at different concentrations, quite irrespective of the value chosen for  $\Delta_0$ . In general, it may be assumed that  $\beta$  will not both increase and decrease with change of concentration at low concentrations. This sets an upper limit to any possible value of  $\Delta_0$ . Whatever value may be chosen for  $\Delta_0$ , however, a change in the value of  $\beta$  is a necessary consequence of the experimental facts. In the following table are given the values for  $\beta$ , for potassium chloride in water at  $18^\circ$  at different concentrations.

TABLE IV.

VALUES OF  $\beta$  AT DIFFERENT CONCENTRATIONS OF POTASSIUM CHLORIDE IN WATER AT  $18^\circ$ .

Assuming  $\Delta_0 = 130.0$ .

$V$ .	$5 \times 10^4$ .	$2 \times 10^4$ .	$10^4$ .	$5 \times 10^3$ .	$2 \times 10^3$ .	$10^3$ .
$\beta \times 10^{-3}$ .....	1.578	1.678	1.700	1.757	1.954	2.201
$V$ .	$5 \times 10^2$	$2 \times 10^2$	$10^2$	50	20	10
$\beta \times 10^{-3}$ .....	2.384	2.526	2.874	3.049	3.260	3.833

It will be observed from this table that, as the concentration increases, the value of  $\beta$  increases markedly up to a concentration of 0.1 *N*. It is obvious, also, that in the case of non-aqueous solvents the variation of  $\beta$ , with increasing concentration, is much greater than it is in the case of aqueous solutions of potassium chloride. Furthermore, in solvents of low dielectric constant, the value of  $\beta$  at high concentration must ultimately decrease as the concentration increases, as may be seen from an inspection of the curve for potassium iodide in sulfur dioxide at  $+10^\circ$ , as shown in Fig. 4.

In the following table are given the calculated values of the constant  $\beta$  for solutions of typical salts in a number of different solvents, derived from the best straight line that may be drawn through the experimental points at low concentrations.

TABLE V.  
VALUES OF  $\beta$  FOR SOLUTIONS OF SALTS IN DIFFERENT SOLVENTS.

Solvent	H <sub>2</sub> O	epichlorohydrin	NH <sub>3</sub>	NH <sub>3</sub>	NH <sub>3</sub>	SO <sub>2</sub> (-33°)	SO <sub>2</sub> (+10°)	C <sub>2</sub> H <sub>4</sub> Cl
Electrolyte	KCl	NEt <sub>4</sub> I	KNO <sub>3</sub>	AgI	KI	KI	KI	NPr <sub>4</sub> I
$\beta \times 10^{-3}$	3.620	9.390	12.63	25.44	7.867	13.63	19.44	20.78

From an inspection of this table it is clear that  $\beta$  is in no sense a constant for solutions of different electrolytes in a given solvent, or for solutions of a given electrolyte in different solvents, or for a given solvent at different temperatures.

Those assumptions in Ghosh's theory which lead to the result that  $\beta$  is a constant are in contradiction with the experimental facts, and must, therefore, be modified or discarded. The actual determination of the value of  $\beta$ , according to Ghosh, depends on an evaluation of the potential of the field due to the ions. In order to evaluate this potential, he finds it necessary to ascribe to the ions not only certain definite charges, but also certain definite fixed positions in the medium. Since, now,  $\beta$  varies as a function of temperature and concentration, as well as of the nature of the solvent medium and the dissolved electrolyte, it follows that, in order to account for the variation in  $\beta$ , it is necessary to discard the assumption that the ions occupy a fixed position in the medium, independent of temperature and concentration. If this assumption is dropped, it obviously becomes impossible to calculate the potential due to the field of the ions in the medium, unless some other hypothesis is made with regard to the distribution of the charges. If the charges do not occupy a fixed position but a variable position dependent upon both temperature and concentration, it appears that we must necessarily revert to a kinetic interpretation of the state of the ions in the solution. The distribution of the ions, therefore, must be determined according to a kinetic hypothesis, taking into account the influence of the charges upon the distribution of the particles in the medium and their motion relative to one another.

### 8. Theoretical Considerations.

Ghosh assumes that all ions having a kinetic energy above a certain critical value are effective in transmitting the current through a solution. In determining the fraction of the ions having a velocity above a given value, he assumes Maxwell's law for the distribution of velocities.<sup>17</sup> The application of Maxwell's law of the distribution of velocities to a system of charged particles, and particularly to a system of charged particles, subject to restriction as regards their positions relative to one another, appears a doubtful procedure, since, at best, Maxwell's law of distribution cannot be expected to hold save in the case of systems free from constraints.

It is a weakness of Ghosh's theory that it is not able to render an account of those properties of electrolytes which depend on the nature of the electrolyte itself. This defect is inherent in the fundamental assumption that electrolytes are completely ionized and that the work involved in the ionization process is purely electrical in nature. That the work done against the electrical forces is a large factor in the ionization process is not to be doubted, but we have no certainty that electrical forces are the only ones involved. At any rate, it is very difficult to account for the properties of different electrolytes on the basis of this assumption. It would seem that the different ionization values for different electrolytes could be accounted for satisfactorily only by assuming forces other than of purely an electrical nature to exist between the various constituents present in the solution, or, rather, that the forces involved do not all obey the inverse-square law. The properties of electrolytic solutions appear to be much too varied in their nature to admit of being accounted for by hypotheses as simple as those underlying Ghosh's theory. While Ghosh has pointed out a method of attacking the problem of electrolytic solutions, it is necessary to modify his postulates as to the distribution of the charges in the medium and as to the determination of the number of carriers which are effective in transporting the current. The problem to be solved is to determine, by means of kinetic considerations, the equilibrium in a system of charged particles and electrical doublets.

In treating osmotic phenomena, Ghosh applies Clausius' Virial Theorem. This theorem leads to results of the first order of approximation only, in the case of ordinary gases, as has been pointed out by Jeans.<sup>18</sup> Its application to a system of charged particles subject to constraints is certainly open to question. At any rate, Ghosh's equation for  $i$  is not in harmony with experiment.

In calculating the potential due to the field in a solution of a binary

<sup>17</sup> Ghosh, Ref. 5, p. 450. Compare Chapman and George, *Phil. Mag.*, **41**, 799 (1921).

<sup>18</sup> Jeans, "Dynamical Theory of Gases," 2 Ed., p. 147.

electrolyte, Ghosh assumes the work necessary to separate a pair of univalent ions to be  $E^2/Dr$ , the medium between the particles being assumed to act normally. In determining, now, the work required to carry one mol of a binary electrolyte from its condition at a given concentration to a condition in which the particles are separated to such distances that the force between them may be neglected. Ghosh evaluates  $r$  on the assumption that positive and negative particles are distributed in a fixed manner throughout the solution, forming a cubical space lattice. From this he derives the expression

$$r = \left( \frac{V}{2N} \right)^{1/3};$$

and substituting this in the expression for the work above, and multiplying by  $N$ , the number of pairs of positive and negative particles, he evaluates the potential due to the assumed distribution of the charges in the medium. It appears, however, that in this procedure Ghosh has taken account of the work due to the separation of the  $N$  pairs of positive and negative particles in the solution, leaving out of account the forces acting between a given charge and all other charges. It is true that Ghosh assumes that the electrolyte forms doublets, but this assumption is inconsistent with the assumptions made in evaluating  $r$ , the distance between the charges.

### Summary.

1. The equation of Ghosh expressing the conductance of electrolytic solutions as a function of the concentration is compared with the experimental values in aqueous and non-aqueous solutions.

2. Plotting values of  $\log \Lambda$  against those of the cube root of the concentration, the experimental points lie upon a curve concave toward the axis of concentrations at low concentrations and convex toward this axis at high concentrations. If Ghosh's equation were applicable, the points should lie upon a straight line. The deviation of the points from a linear relation is consistent throughout, and cannot be accounted for by errors in the original observations. In its present form Ghosh's theory does not satisfactorily account for the properties of electrolytic solutions.

3. The postulates and assumptions underlying Ghosh's theory are briefly discussed, and some inconsistencies are pointed out.



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. I, 8.]  
**THE CONDUCTANCE OF CONCENTRATED SOLUTIONS OF  
SODIUM AND POTASSIUM IN LIQUID AMMONIA.**

BY CHARLES A. KRAUS AND WALTER W. LUCASSE.

Received September 10, 1921.

**1. Introduction.**

In a series of articles,<sup>1</sup> it has been shown that the conduction process in solutions of the alkali metals in liquid ammonia is ionic. The positive ion in these solutions is identical with the positive ion of a salt of the same metal, while the negative ion is apparently the negative electron. At low concentrations the negative electron is associated with ammonia, as a consequence of which its speed is of the order of magnitude of that of normal ions; for example, in sodium solutions the speed of the negative ion is 7 times that of the sodium ion. At higher concentrations, however, the carrying capacity of the negative ion increases. This is due to an increase in the speed of this ion in consequence of its loss of ammonia at higher concentrations. At very high concentrations, the speed of the negative ion in ammonia is comparable with that of the ions in metals, since the conductance of the metal solutions in ammonia reaches very high values. In previous investigations the conductance has been measured up to concentrations as high as 2.0 *N* with a preliminary observation on the conductance of a saturated solution of sodium in ammonia, the specific conductance of which is approximately one-half that of mercury. It is of interest to examine in detail the conductance curve in the concentrated regions, and, furthermore, to compare the conductance curves of different metals in this region. If the conductance of the concentrated solutions is due to the negative electron, which is therefore the same in solutions of different metals, then we might expect that the conductance curves of different metals in very concentrated solutions will resemble one another quite closely. In the present investigation the conductance of concentrated solutions of sodium and potassium has been studied.

**2. Method, Apparatus and Manipulation.**

Since the conductance of concentrated solutions of the metals in ammonia approaches that of mercury, it is obvious that special means must be adopted in order to measure its value. The ordinary methods, in which a pair of electrodes is introduced into a solution, obviously fail, since the resistance of these solutions is too low to be measured by such means. The apparatus finally employed in this investigation is the same as that employed by Kraus at an earlier date.<sup>2</sup> This apparatus is shown in outline in Fig.

<sup>1</sup> Kraus, *THIS JOURNAL*, 30, 1323 (1908); 36, 864 (1914); 43, 749 (1921).

<sup>2</sup> Kraus, *ibid.*, 43, 757 (1921).

1. The function of its various parts will, perhaps, be best understood by following the procedure in the case of a typical run.

Referring to the figure, Stopcock A connects the apparatus with a high vacuum system. On opening this cock, the entire apparatus, with the exception of the conductivity cell itself, which is shut off by means of the stopcocks B and C, is thoroughly

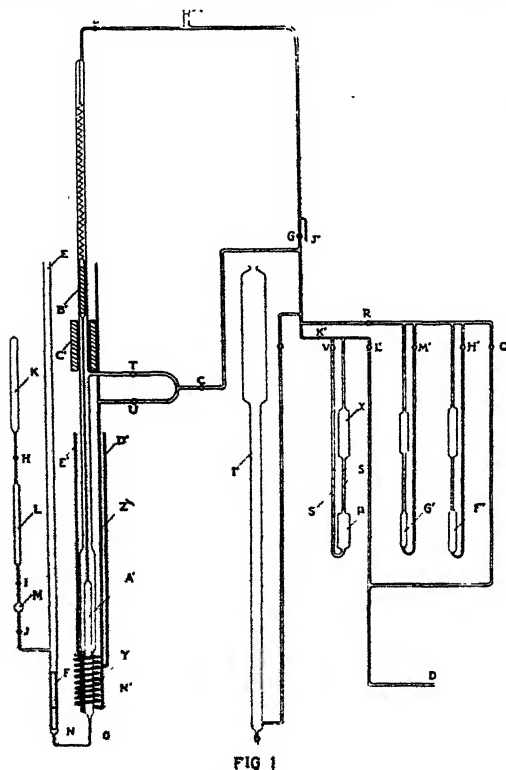


Fig. 1.—Outline of conductivity cell and measuring devices.

exhausted. When a sufficiently high vacuum has been obtained, this part of the system is filled with ammonia vapor which passes through K', L', Q and R from a supply cylinder, which is not shown in the figure but which is attached at D. The metal, the conductance of whose solutions is to be measured, is freshly cut and rolled into the form of cylinders of suitable size and introduced into the tube E with a glass weight F placed upon it. The tube is then sealed off at E and, after closing the stopcock G, the conductance cell is thoroughly evacuated through B. Stopcocks A, B, and G are then closed, C is opened, and the entire system is filled with ammonia from the supply tank. The stopcocks H, I and J are then closed, trapping ammonia in the tubes K, L, and M. Stopcock G remaining closed, A and B are opened, thus making connection with the vacuum system. When the conductance cell has been thoroughly evacuated, a bath of paraffin oil is placed around the lower part of the cell and that part of the tube E which contains the metal. The temperature of the bath is raised to about 10° above the melting point of the metal. When the metal is completely melted, the stopcock J is opened and ammonia is allowed to enter the tube E. Thus there is a slight pressure of ammonia gas in E which forces the metal through the capillary tube N into the conductance cell. In most cases this initial pressure is sufficient to force the metal through the capillary, but when this is not so, additional ammonia may be obtained from the chambers L and K and introduced into E in suitable amounts. As a rule, it is well to force the metal over with as small a pressure as possible in order to avoid spattering the molten metal on the upper walls of the cell. When the metal has been transferred, the last traces of ammonia are withdrawn with a pump, and the capillary is sealed off at O, while the filling tube OE is removed. When the sealing operation is concluded, the stopcocks A and B are shut off and the entire apparatus is filled with ammonia through C.

As was stated above, D is joined to a supply cylinder containing pure ammonia. In

preparing the solutions in the conductivity cell, ammonia is distilled from the supply cylinder into the measuring cell P, which has a capacity of approximately 5 cc. A vacuum-jacketed tube containing ammonia is placed around the cell P, while the stopcocks Q and R are kept closed and L' V and K' open. During this operation, connection with the conductance cell is shut off at C and G. The quantity of ammonia introduced into P, and later into the conductance cell, is measured along the scales on the tubes SS. These scales each have a capacity of about 0.5 cc. and are graduated in 0.01 cc. A third decimal place is obtained by estimating the tenths of the scale divisions. The measuring cells G' and F' are similar, except that one arm of these cells consists of a capillary. G' and F' have capacities of 1.25 and 2.5 cc. respectively.

After determining the volume of liquid in the measuring cell P, stopcocks T, G and V are closed and C and U opened, while the ammonia bath surrounding P is removed and replaced by a source of heat. At the same time the conductivity cell is surrounded by a bath of liquid ammonia. Under these conditions, ammonia evaporates in P and condenses on the metal in the conductivity cell. The purpose of the stopcock V is to force the boiling ammonia through the vaporizing chamber X and also to facilitate the boiling process. Without this stopcock, super-heating is liable to take place and, if the pressure becomes excessive, solvent may be lost either by blowing out one of the stopcocks or by blowing out through the mercury trap I'.

The initial quantity of approximately 5 cc. of ammonia condensed in the conductivity cell is not sufficient to bring the level of the liquid above the opening of the capillary Y. For this purpose, the cell is provided with a displacement cylinder which may be lowered by means of the external solenoid C'. The displacer consists of the glass cylinder A' which is connected by a glass rod to a glass-encased soft iron core B' which is suspended by means of a platinum-iridium spring. This device serves to raise the level of the liquid in the conductivity cell as well as to stir the solution in order to insure a uniform concentration throughout. With the displacement cylinder at its lowest position, the initial charge of ammonia is sufficient to fill the cell to a point where the electrodes are covered. The resistance of the liquid is measured in the glass spiral Y, consisting of 14 turns of capillary tubing, one end of which is connected to the cell at the point shown in the figure and the other end of which is connected to the lower extremity of the tube Z. One electrode, which consists merely of about 1.5 mm. of platinum wire, is introduced near the lower end of the tube Z, while another similar electrode is introduced near the lower end of the main chamber of the conductivity cell. Thus, the current passes through the solution in the cell and through the capillary whose length is approximately one meter and diameter somewhat less than a millimeter. The platinum electrodes are unplatinized, since these solutions do not polarize and platinum black tends to catalyze the reaction between the metal and the solvent. Copper leads are introduced into the wells D' and E' containing mercury, thus making connection with the platinum wires which serve as electrodes.

The resistance was measured by the usual Kohlrausch method, employing a small induction coil or an oscillator as a source of alternating current. The resistance of the lead system was carefully determined beforehand and allowed for in the final calculations.

Due to the difference in diameter of the tube Z and the capillary at N', bubbles of ammonia vapor are liable to form at this point. In order to avoid this difficulty at times, it is necessary to close the stopcock U and introduce a slight additional pressure upon the solution through T. The ammonia required to furnish this additional pressure is obtained from the measuring cell P, which has been filled in the meantime. The amount of ammonia so introduced is read off the graduated scales SS. When a satisfactory reading of the resistance of the initial solution has been obtained, ammonia is condensed in the cell G', the exact amount of liquid condensed being read off on the

graduated stem. This cell, like cell P, as well as the cell F', is provided with a vaporizing chamber and a control stopcock M', corresponding to V. The method of manipulation is entirely similar to that already described in connection with cell P. When a sufficient number of points have been obtained with volume additions of approximately 1.25 cc., ammonia is condensed in the cell F', whose volume is approximately 2.5 cc. After obtaining a number of observations with F' as measuring cell, the volume of the solution in the conductivity cell becomes sufficiently large so that further additions may be made directly from the cell P. The manometer I' serves to show the pressure under which ammonia is being condensed and also as a manometer for the purpose of determining the vapor pressure of the solutions. When a run is completed, the bath surrounding the conductivity cell is removed and the tip J' is broken off, thus allowing the ammonia in the cell to escape. At the same time a small amount of ammonia vapor is passed through C and U, and through the coil Y. By this means, the capillary is kept free from metal. Without this precaution, the capillary is filled with metal from which it can be freed only with great difficulty. When the ammonia has completely evaporated from the cell through J', this tip is again sealed, stopcocks C and G are closed, and the cell is thoroughly evacuated through B. When all traces of ammonia vapor have been removed, the tip J' is again broken and the tip O at the bottom of the cell is likewise broken off. Absolute alcohol, in the case of sodium, and absolute ether, with small additions of absolute alcohol, in the case of potassium, are then drawn into the conductance cell through O by suction applied at J'. By suitably manipulating the stopcocks B, G, C and U, the solvent may be drawn to any desired height in the cell or the capillary. When the metal has been completely dissolved, the cell is thoroughly washed with distilled water. The original solution of the metal, together with the wash waters, are combined, and the whole is titrated with standard acid.

The measuring cells were calibrated by first weighing empty and then filled with distilled water up to a height noted on the scale. In calculating the amount of ammonia used from cells F' and G', account was taken of the difference in the capillary rise of ammonia and water in the capillaries forming the right arm in each case. The volume of the capillary was also taken into consideration when the relative height of the liquid in the two arms was other than that at which the cell had been calibrated. Correction was also made for ammonia in the vapor space of the conductivity cell when this was found necessary.

The ammonia<sup>3</sup> was run directly into auxiliary cylinders having a capacity of 1 or 2 kg., into which about 3 g. of sodium had previously been introduced. After having withdrawn sufficient ammonia from the auxiliary cylinder so that it was practically free from hydrogen, the small supply cylinder mentioned above was connected to it and from 150 to 200 g. of ammonia was distilled into it. Previously, about 0.25 g. of sodium had been introduced into this cylinder also. As stated, this cylinder was joined to the apparatus at D. Thus the solvent was purified by being twice distilled from a sodium solution.

The sodium<sup>4</sup> was freshly cut before introducing into the tube E. By so doing, and by rapid manipulation, the formation of oxide is avoided. In the case of potassium it was found preferable to cut the metal under light petroleum ether.

One of the most probable sources of inconsistencies in the results is due to the possible lack of uniformity in the concentration of the solutions. Since the resistance changes very rapidly as the concentration changes, it follows that a slight change in the amount of ammonia in the capillary

<sup>3</sup> Obtained from the National Ammonia Company.

<sup>4</sup> From the Solvay Process Company.

Y would cause a considerable change in the measured specific conductance. This source of error was not completely eliminated and, in all likelihood, variations in the measured values obtained are due chiefly to this cause. This error may run as high as 1% for individual observations.

Since the density of the solutions is not known, the dilution  $V$  is expressed in liters of pure solvent per gram atom of metal. As the volume of the ammonia at its boiling point was measured directly, the density enters only in calculating corrections. For this the value 0.674 was assumed.

### 3. Calibration of the Conductance Cell.

The specific conductance of the solutions was determined by direct comparison of the resistance of the solutions with that of mercury. The mercury employed for this purpose was initially cleaned with sand, then with nitric acid, and finally it was twice distilled. The cell, after introducing the mercury, was placed in a bath of water at  $20^\circ$  and the resistance determined in the usual way. The resistance of the mercury in the capillary, after making correction for the resistance of the leads, was found to be 2.693 ohms at  $20^\circ$ . The specific conductance of the solutions at the boiling point of liquid ammonia was then calculated by means of the equation,  $l_x = R'l'/R_x$ , where  $l'$  is the specific conductance of mercury at  $20^\circ$ ,  $R'$  the resistance of mercury in the cell at  $20^\circ$ , and  $R_x$  the resistance of the solution in the cell at  $-33.5^\circ$ . When the cell is placed in liquid ammonia, the leads are at a temperature of  $-33.5^\circ$  at their lower extremity, while at room temperature at the top. Knowing the resistance of the leads and the temperature coefficient of the metal, correction was made for this effect. The specific conductance of mercury at  $20^\circ$  was assumed to be  $1.0444 \times 10^4$ .

### 4. Experimental Results.

The results obtained for the conductance of concentrated solutions of sodium and potassium in liquid ammonia are given in Tables I and II,

TABLE I.  
SPECIFIC CONDUCTANCES OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT VARIOUS DILUTIONS AT  $-33.5^\circ$ .

Run 2.			Run 3.		
No.	V.	$l$ .	No.	V.	$l$ .
1	0.1081	5047	1	0.1626	3356
2	0.1200	5047	2	0.1698	3023
3	0.1331	4954	3	0.2099	1945
4	0.1440	4348	4	0.2510	1288
5	0.1444	4394	5	0.3210	726.2
6	0.1560	3718			
7	0.1681	3166			
8	0.1804	2687			
9	0.1926	2347			
10	0.2652	1174			
11	0.2761	1080			
12	0.2768	1070			
			Run 5.		
No.	V.	$l$ .	No.	V.	$l$ .
			1	0.3463	575.3
			2	0.4393	275.8

TABLE I (*continued*).

Run 4.			Run 6.		
No.	V.	<i>l.</i>	No.	V.	<i>l.</i>
1	0.1616	3167	1	0.3393	612.8
2	0.2042	1981	2	0.4262	297.6
3	0.2470	1344	3	0.5099	148.3
4	0.3230	714.4	4	0.5933	79.56
5	0.4011	379.9	5	0.7612	20.21
6	0.5772	92.19	6	0.9265	5.988
7	0.7527	22.95	7	1.298	1.269
8	0.9263	6.493	8	1.674	0.6456

respectively. At the top of each sub-table is given the number of the run. In the first column is given the number of the point in the run; in the second column, the dilution *V* in liters of solvent per gram atom of metal; and, in the third column, the specific conductance in reciprocal ohms. A number of runs, which were obviously in error, have been omitted.

TABLE II.

SPECIFIC CONDUCTANCES OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AT VARIOUS DILUTIONS AT  $-33.5^{\circ}$ .

Run 1.			Run 2.		
No.	V.	<i>l.</i>	No.	V.	<i>l.</i>
1	0.1572	2940	1	0.0853	4569
2	0.2004	1858	2	0.1058	4560
3	0.2418	1288	3	0.1295	4190
4	0.3157	701.4	4	0.1519	3233
5	0.3891	389.8	5	0.1730	2571
6	0.5577	91.16	6	0.2103	1772
7	0.7229	21.69	7	0.2466	1278
			8	0.3317	640.7
			9	0.4194	318.8

## 5. Discussion.

In Fig. 2 are shown values of the logarithms of the specific conductance of sodium solutions plotted as ordinates against values of the logarithms of the dilution plotted as abscissas. The values of Run 2 are represented by circles, those of Run 3 by crosses, those of Run 4 by combined circles and crosses, those of Run 5 by squares and those of Run 6 by broken crosses. In order to compare the results here obtained with those in the more dilute solutions previously measured by Kraus, a few values from the earlier investigation have been added on the figure, being represented as broken vertical lines. As may be seen, the two are in excellent agreement. In Fig. 3 the heavy curve passing through the points is that of potassium solutions, while that of sodium solutions is represented as a lighter line. Here, again, the results of Run 1 are represented by circles and those of Run 2 by crosses, while the earlier values of Kraus are represented by broken vertical lines.

The first few points on the curve at the highest concentrations lie on a horizontal straight line. These points give the conductance of solutions saturated with the metal. The points of intersection between the horizontal portions and the other branches of the curves represent saturated solutions. The concentrations of the saturated solutions may therefore be obtained from these curves. On making the necessary calculations

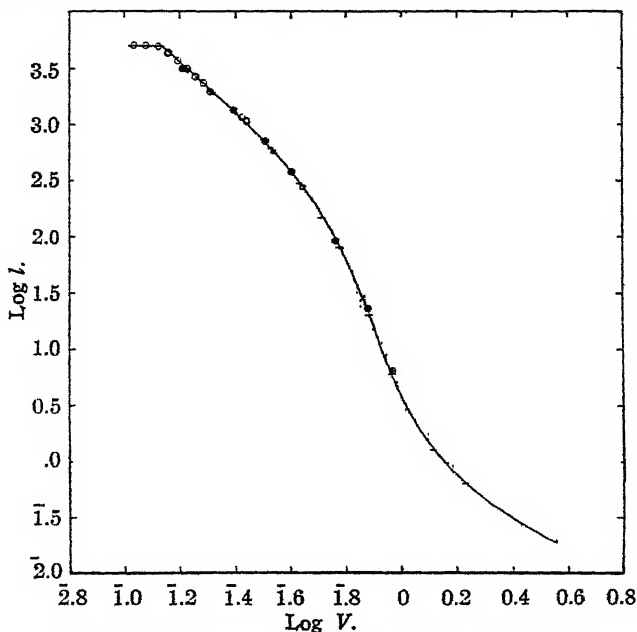


Fig. 2.—Conductance curve for solutions of sodium in ammonia.

it is found that one atom of sodium is dissolved in 5.367 molecules of ammonia, and that one atom of potassium is dissolved in 4.866 molecules of ammonia. The agreement with the determinations of Ruff and Geisel<sup>5</sup> is fairly good. Taking into account the difficulties involved in the direct determination of the solubility by the method of Ruff and Geisel, it would appear that the present results are the more reliable.

The value obtained for the specific conductance of the more concentrated solutions of sodium and potassium in liquid ammonia is a very striking result. The specific conductance of a saturated sodium solution is 5047.0, while that of a saturated potassium solution is 4569. The sodium solutions conduct slightly better than the potassium solutions. The specific conductance of mercury at 20° is  $1.044 \times 10^4$  from which it is evident that the value of the conductance of these solutions is comparable with that of the metals. However, in making such a comparison the values of the

<sup>5</sup> Ruff and Geisel, *Ber.*, 39, 828 (1906).

atomic, rather than those of the specific, conductance should be compared. In Table III are given values of the atomic conductance of various metals at 0° or near room temperatures.<sup>6</sup>

TABLE III.  
ATOMIC CONDUCTANCES OF METALS.

Metal.	Atomic conduct- ance. $\Lambda \times 10^{-4}$ .	Metal.	Atomic conduct- ance. $\Lambda \times 10^{-4}$ .
Silver.....	6.999	Tantalum.....	1.339
Potassium.....	6.503	Tin.....	1.252
Sodium.....	5.288	Osmium.....	1.119
Rubidium.....	4.845	Tellurium <sup>a</sup> .....	1.052
Copper.....	4.559	Thallium.....	0.9778
Gold.....	4.547	Nickel.....	0.9613
Cesium.....	3.898	Lead.....	0.9222
Aluminum.....	3.834	Palladium.....	0.9082
Titanium (N <sub>2</sub> ).....	3.345	Platinum.....	0.8314
Magnesium.....	3.215	Iron.....	0.8031
Chromium.....	2.989	Strontium <sup>a</sup> .....	0.7194
Calcium, 99.5%.....	2.457	Cobalt, 99.8%.....	0.7064
Indium.....	1.905	Manganese (N <sub>2</sub> ).....	0.6561
Cadmium.....	1.875	Antimony.....	0.4658
Rhodium.....	1.811	Arsenic.....	0.3735
Zinc.....	1.713	Gallium.....	0.2208
Lithium.....	1.534	Bismuth.....	0.1972
Iridium.....	1.414	Mercury.....	0.1564
		Saturated sodium sol. <sup>b</sup> .....	0.6720

<sup>a</sup> Calculated on the assumption that the conductance of silver amounts to  $60 \times 10^4$ .

<sup>b</sup> Calculated on the assumption that the density of the solution is equal to that of the pure solvent. The density is actually less than that of the solvent. The value given for  $\Lambda$  is therefore less than the true one.

The atomic conductance of a saturated solution of sodium in liquid ammonia is  $0.672 \times 10^6$ . It is evident that the atomic conductance of saturated solutions of sodium and potassium in liquid ammonia is of the order of that of such metals as strontium and iron, and much greater than that of mercury and bismuth. If the conductance measurements could be extended into the supersaturated regions, it is evident, from the form of the curves, that much larger values of the atomic conductance might be expected. It is interesting to note that, as may be seen from the table, those elements which exhibit the highest atomic conductance all belong to the first group of elements. Among the elements having an atomic conductance greater than  $1.5 \times 10^6$ , all belong to the first three groups of elements, with the exception of rhodium, chromium and titanium.

The manner in which the conductance varies as a function of the con-

<sup>6</sup> Landolt-Börnstein "Physikalisch-Chemische Tabellen," 1912.



centration is very interesting. At the highest concentrations, the specific conductance increases approximately five fold, when the concentration is doubled. In this region, the relation between the specific conductance and the concentration may be expressed by an exponential equation, since the logarithm of the specific conductance varies very nearly as a linear function of the logarithm of the dilution, as may be seen from Fig. 2. At somewhat lower concentrations, the conductance curve is concave toward the axis of concentrations, after which it exhibits an inflexion point at about  $V=0.65$ . In this region the specific conductance of the solution increases enormously with the concentration. Between  $V=0.5933$  and

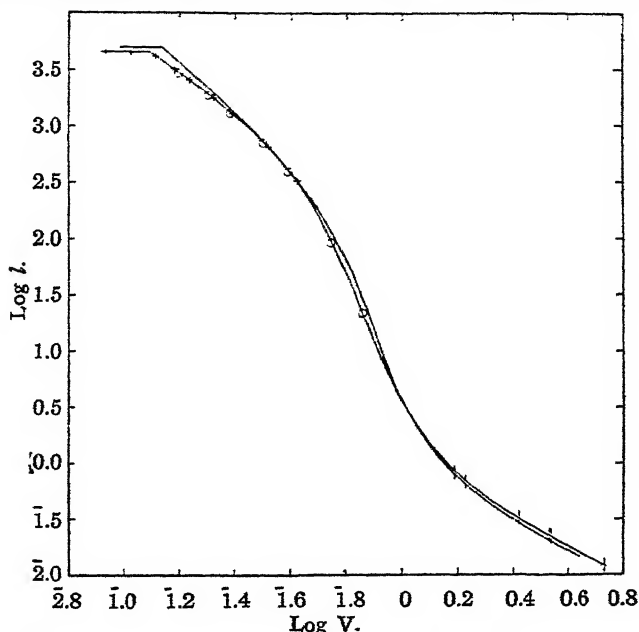


Fig. 3.—Comparison of conductance curves for potassium and sodium in ammonia.

$V=0.3393$  the conductance increases from 79.56 to 612.8 or nearly 10-fold, while between  $V=1.298$  and  $V=0.5933$  the conductance increases from 1.269 to 79.56 or more than 60-fold. In the neighborhood of  $V=0.67$  a concentration increase of 1% is accompanied by a conductance increase of approximately 15%. It is in these regions that the negative electrons are becoming free from the ammonia molecules with which they are associated in the more dilute solutions. At higher concentrations this factor is doubtless of smaller influence, and it is possible that a change in the total number of carriers present has a material influence on the conductance.

Very striking, is the great similarity of the curves for sodium and potas-

sium. Indeed, they almost coincide over a considerable range of the concentration interval. In the most concentrated solutions the conductance of potassium is somewhat lower than that of sodium. The two curves then coincide, after which again they diverge slightly at a value  $\log V = 1.7$ . Thereafter they again intersect and diverge slightly at lower concentrations owing to the greater conductance of the potassium<sup>7</sup> ions. Apparently, the specific conductance of the more concentrated sodium and potassium solutions is very nearly the same at the same equivalent concentration. When we take into account the fact that the densities of the two solutions probably vary appreciably<sup>8</sup> and that, furthermore, the solvation of the positive ions in all likelihood differs for the two metals, it is remarkable that the two curves should approach each other so closely. This is merely an expression of the fundamental fact that the conductance of these solutions is due to the same cause; namely, to the negative electron. It would appear from this, that both the number of electrons and the speed with which they move in these solutions is a function primarily of the equivalent concentration. Since it has previously been shown that the negative carrier in dilute solutions of different metals in ammonia is the same, and since it has been shown that the increase in conductance with increasing concentration is due to the increased speed of the negative carriers in these solutions, it follows that the conductance of the concentrated solutions is due to a common negative carrier, obviously the negative electron. Moreover, since the order of the conductance of these solution is the same as that of the metals, the conclusion appears justified that the conduction process in metals consists essentially in a motion of the negative electron.

## 6. Summary.

1. The specific conductance of solutions of sodium and potassium in liquid ammonia at its boiling point has been measured from concentrations in the neighborhood of normal up to the saturation point.

2. As the concentration increases, the specific conductance increases enormously, reaching the values  $0.5047 \times 10^4$  and  $0.4569 \times 10^4$  for saturated solutions of sodium and potassium respectively.

<sup>7</sup> Kraus, *THIS JOURNAL*, 43, 749 (1921).

<sup>8</sup> In respect to density, these solutions are most exceptional. While no exact quantitative data have yet been obtained, the order of magnitude of the volume change may be seen from the following observation. The level of the solution at the third point in the second run with potassium was noted and, when the run was completed, the volume of the cell up to this height was obtained roughly by filling it with water. The amount of metal was of course known and the volume of ammonia at this point was likewise known. From these data the density of this solution was calculated to be 0.632. How abnormal these solutions are is realized on noting that 2.48 g. of a solid of density 0.86 and 5.55 g. of a liquid of density 0.674 form a solution of density 0.632.

3. The specific conductance of solutions of sodium and potassium at the same equivalent concentration is very nearly the same.

4. The equivalent conductance of saturated solutions of sodium and potassium in liquid ammonia is of the order of magnitude of that of such metals as strontium and iron.

5. The solubility of sodium and potassium in liquid ammonia at its boiling point has been found to be 5.367 and 4.866 mols of ammonia per atom for sodium and potassium respectively.

6. The results of this investigation furnish further evidence in support of the hypothesis that the conduction process in metals consists in a motion of negative carriers of sub-atomic dimensions, which carriers are the same for all metals.

WORCESTER, MASSACHUSETTS.

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN.]

## THE PREPARATION AND PROPERTIES OF THE PERSULFIDES OF HYDROGEN.

BY JAMES H. WALTON AND LLEWELLYN B. PARSONS.

Received September 20, 1921.

### Introduction.

When an excess of hydrochloric acid is added to a solution of a polysulfide of an alkali or one of the alkaline earths, a yellow oily liquid separates. Since the time of Scheele, who first prepared this substance, much work has been done on its preparation and the study of its properties. Among the more recent investigators, the work of Rebs,<sup>1</sup> Bruni and Borgo,<sup>2</sup> and Bloch and Höhn<sup>3</sup> are worthy of note. The experiments of the latter authors are the most important in connection with this investigation. These investigators prepared the yellow oil by dissolving sulfur in a solution of sodium sulfide contained in a flask through which a stream of hydrogen was passed to prevent oxidation. The resulting solution was chilled and then run into a hydrochloric acid mixture consisting of one part of hydrochloric acid and one part of ice, surrounded by a mixture of ice and salt. Operating in this way they obtained a product with a density varying from 1.62 to 1.69. The yellow oil when subjected to fractional distillation, yielded two products which on analysis gave the empirical formulas  $H_2S_2$  and  $H_2S_3$ . Further experiments confirming the work of Bloch and Höhn were carried out by Schenck and Falcke.<sup>4</sup>

<sup>1</sup> Rebs, *Ann. Chem.*, **246**, 356 (1888).

<sup>2</sup> Bruni and Borgo, *Gazz. chim. ital.*, **38**, 279, 292 (1907-8).

<sup>3</sup> Bloch and Höhn, *Ber.*, **41**, 1961 (1908).

<sup>4</sup> Schenck and Falcke, *Ber.*, **41**, 2600 (1908).

The object of the present investigation was to improve the method for the preparation of the pure persulfides, and to study the chemical and physical properties of these compounds.

### Experimental.

**Preliminary.**—To determine the effect of the common acids on a solution of sodium polysulfide, a solution of this substance similar to that used in the following experiments was prepared. This was cooled and slowly run into solutions of acetic, phosphoric, sulfuric, and hydrochloric acids respectively. Hydrochloric acid brought about the formation of the yellow oil; the other acids gave complete decomposition into sulfur and hydrogen sulfide.

**The Preparation of the Crude Persulfide.**—The methods given in the literature for the preparation of this substance are vague and difficult to repeat, many essential details being omitted. As a consequence, the modified method used by the authors is given in detail. Two kg. of commercial C. P. sodium sulfide crystals was placed in a 3-liter round-bottomed flask, 300 g. of flowers of sulfur added, and the two thoroughly mixed. Eight hundred cc. of water, enough to dissolve completely the resulting polysulfide at room temperature was then added. The flask was closed with a Bunsen valve, which obviates the necessity of passing hydrogen through the solution, and then heated on a water-bath for from 3 to 4 hours with occasional shaking. At the end of this period all the sulfur was dissolved. This polysulfide solution can be kept in a tightly stoppered vessel for several weeks without deteriorating sufficiently to influence the subsequent operations.

Preliminary experiments showed that cold hydrochloric acid, sp. gr. 1.19, was satisfactory for decomposing the sodium polysulfide. The cooling and rate of bringing the two solutions together are of great importance. Fig. 1 illustrates the apparatus used for this purpose. A and A' are galvanized iron containers insulated by excelsior. C is a specimen jar, diameter 25 cm. This was surrounded by a mixture of ice and salt. Three liters of the concentrated acid was placed in the jar and agitated with a stirrer driven at the rate of about 100 r. p. m. To aid in the cooling a few pieces of ice were always kept in the hydrochloric acid solution. During the reaction the temperature of the hydrochloric acid was kept between  $-4$  and  $-10^{\circ}$ . The sodium polysulfide was added from E at a rate of about 3 liters per hour. Attention is called to the necessity of adding the polysulfide below the surface of the hydrochloric acid, this procedure minimizing the decomposition of the hydrogen persulfides. After about a liter and a half of the sodium polysulfide had been added, the persulfides began to rise in the form of a dark brown scum, and decompose with the evolution of hydrogen sulfide. At this point the addition of sodium

polysulfide was stopped, the specimen jar was replaced with one containing a fresh portion of hydrochloric acid, and the operation continued until all the sodium polysulfide had been added. The persulfides, which were now largely present as an emulsion, settled on the bottom of the container in about 2 hours. This liquid was separated by means of a separatory funnel and washed several times with cold distilled water. In general 2 kg. of sodium persulfide gave a yield of between 400 and 500 cc. of the crude product.

In drying the crude product obtained above, fused calcium chloride, previously treated with dry hydrogen chloride, had been used by previous investigators. Whenever the calcium chloride was used in this investigation, an appreciable amount of decomposition of the persulfides took place with the evolution of large amounts of hydrogen sulfide.

Phosphorus pentoxide has no action on the persulfides and so was used to dry them. Several g. of this substance was allowed to stand in contact with the yellow liquid for a day or two with occasional shaking. At the end of that time the phosphorus pentoxide was removed by filtering through asbestos on a Büchner funnel. Fused powdered boric oxide may also be used to dry the yellow oil. This substance is inconvenient to prepare and offers no advantages over the phosphorus pentoxide. Analysis of the crude product prepared in this way showed that on decomposing it yielded between 19 and 21% of hydrogen sulfide. The compound  $H_2S_8$  evolves 20.98% of hydrogen sulfide. It is believed, however, that this crude product is a solution of sulfur in equilibrium with various sulfides of hydrogen and not a definite compound. This point will be the subject of further investigation.

**Analysis of the Persulfides.**—No rapid and accurate method for analyzing the persulfides has been described. Among those used may be mentioned (1) the decomposition of the persulfides by heat with subsequent determination of the hydrogen sulfide formed, (2) solution of the persulfide in an organic solvent such as toluene, addition of standard iodine and titration of excess of the iodine, (3) determination of the hydrogen by combustion and the sulfur by the Carius method. The published results of analyses by these methods are far from satisfactory.<sup>8</sup> A long series of

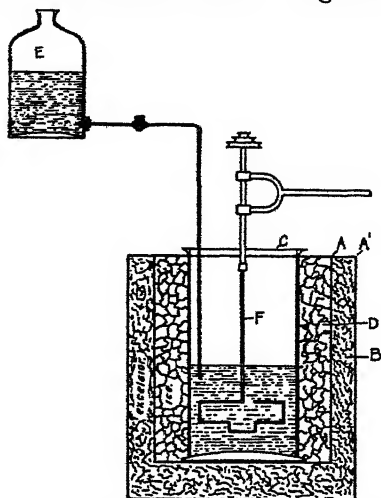


Fig. 1.—Apparatus for preparation of persulfide.

experiments carried out to test Method 2 failed to give concordant results. In the analysis of the persulfides by the determination of the total hydrogen and the sulfur present, small experimental errors introduce very large errors in the empirical formulas computed. The method finally adopted consisted in dissolving a weighed amount of the hydrogen persulfide in carbon disulfide, adding acetone to decompose the persulfide, removing the acetone, carbon disulfide and hydrogen sulfide by evaporation, and weighing the sulfur. The hydrogen sulfide was then found by difference. The details of this method are as follows. Two to three g. of the sample was placed in a tared 75mm. quartz test-tube which was then corked and weighed at once. The tube was nearly filled with carbon disulfide, the contents poured into a tared 75mm. crystallizing dish and the tube washed out with the disulfide. The total volume of disulfide used was 20 to 30 cc. About 10 cc. of pure acetone was then added to the solution and the crystallizing dish covered with a watch glass. After the evolution of gas had ceased, the watch glass was rinsed with disulfide and the solution allowed to evaporate spontaneously, the process being complete in 3 to 4 hours. The residue of rhombic sulfur crystals was dried to constant weight at 90°.

A blank run made by evaporating 50 cc. of the mixed disulfide and acetone gave no weighable residue. The following table shows that the results obtained by this method are independent of the size of the sample and the volume of carbon disulfide used. Ten cc. of acetone was used in each case.

	1.	2.	3.
CS <sub>2</sub> , cc.....	25	50	75
Sample, g.....	2.2945	3.2243	2.1412
Sulfur residue, g.....	1.8476	2.5933	1.7240
H <sub>2</sub> S evolved, g.....	0.4469	0.6316	0.4172
H <sub>2</sub> S in sample, %.....	19.48	19.58	19.49

This extremely accurate and rapid method was used in all the analyses made in this investigation.

**Distillation of the Persulfide.**—The distillation of the crude persulfide yields the compounds H<sub>2</sub>S<sub>2</sub> and H<sub>2</sub>S<sub>3</sub>. The apparatus described by Bloch and Höhn may be used for this purpose; the yields obtained, however, were very unsatisfactory. Ordinary glass decomposes the persulfides of hydrogen, the action being due to the alkali in the glass. At temperatures necessary for distillation the decomposition is considerable. Several investigators have decreased this decomposition by treating the glass with hydrochloric acid. The advantage of quartz apparatus for distillation and also for preservation of the persulfides of hydrogen is shown by the following experiment. A quantity of the crude persulfide was placed in a small Pyrex flask that had been treated with hot conc. hydrochloric acid and dried by passing a stream of dry hydrogen chloride through it. An

equal quantity of persulfide was placed in a clean dry quartz flask and the two allowed to stand under similar conditions for several days. In less than a week the persulfide in the Pyrex flask had decomposed to such an extent that crystals of sulfur were deposited. No sulfur crystals were deposited in the quartz flask after standing for a month.

The apparatus used in Fig. 2 is similar in principle to that of Bloch and Höhn. As far as possible quartz was used in its construction.

B is a 250cc. quartz distilling flask. The inner tube of the condenser, E, is of hard glass, 8 mm. outside diameter. C is a 300cc. quartz flask fitted with a 2-holed paraffined rubber stopper. By means of a hard glass tube it is connected with a 20cm. quartz test-tube which is also fitted with a paraffined rubber stopper. A is a 500cc. hard glass distilling flask.

In carrying out the distillation the flask B was heated to 120° in a glycerine bath and the system exhausted by means of a vacuum pump to a pressure of 3 to 5 mm.

C was cooled by the water from the condenser which ran out through a Y-tube. D was cooled in the first experiments by solid carbon dioxide and ether as described by Bloch and Höhn. Salt and ice mixture was found to be quite satisfactory, however, and this mixture was used in

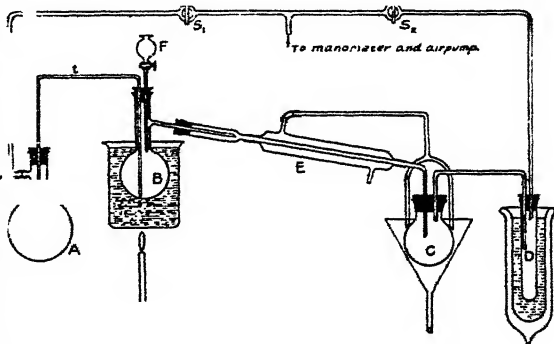


Fig. 2.—Distilling apparatus for persulfides.

the later experiments. Ten to 15 cc. of the crude persulfide was run into B through the separatory funnel, F, whereupon the persulfides began to distil slowly. After 10 minutes the residue in B consisted mainly of sulfur dissolved in persulfide. This was removed by closing the cock  $S_1$  and opening  $S_2$ , whereupon the residue was drawn over into A. Inasmuch as this residue solidifies on cooling, the tube *t* had to be carefully heated during this operation. After the residue had been removed from the flask,  $S_1$  was closed,  $S_2$  opened, more persulfide added, and the distillation carried on as before.

The yield by distilling the crude product depends upon many factors, the most important of which is the age of the sample. Two volumes of the freshly prepared persulfides usually gave 1 volume of distillate;  $\frac{2}{3}$  of this was hydrogen trisulfide and  $\frac{1}{3}$  hydrogen disulfide.

In the later experiments it was found that a vacuum of 20 to 25 mm. could be used in the above distillation; as a consequence a water suction pump can be used with entire satisfaction.

**Hydrogen Trisulfide.**—This substance collects in Receiver C in a high state of purity, as is shown by the following results of analysis.

	1.	2.	3.
Sample, g.....	2.8576	1.7875	3.7798
Sulfur residue, g.....	1.8727	1.1740	2.4838
H <sub>2</sub> S evolved, g.....	0.9848	0.6135	1.2960
H <sub>2</sub> S in sample, %.....	34.46	34.42	34.28
Calculated H <sub>2</sub> S in H <sub>2</sub> S <sub>3</sub> , %.....	34.69	.....	.....

Hydrogen trisulfide is a mobile, yellow, oily, liquid with an odor similar to that of camphor and sulfur monochloride. Its vapors attack the eyes and nose strongly. On cooling the trisulfide, the yellow color disappeared, this behavior being exactly analogous to that of yellow rhombic sulfur which becomes pure white at the temperature attainable with solid carbon dioxide snow and ether. The trisulfide was soluble in benzene, toluene, chloroform, carbon disulfide, ether, and heptane, while alcohols, ketones, nitrobenzene, aniline and pyridine caused it to decompose catalytically. In any of the above mentioned solvents it was noted that small quantities of impurities caused the trisulfide to decompose with the deposition of white gleaming crystals of nacreous sulfur which, on standing changed rapidly into ordinary rhombic sulfur.

To determine the melting point of the trisulfide, some of it was cooled in a bath of carbon dioxide snow and ether to a temperature of  $-78^{\circ}$  as registered on a toluene thermometer. On cooling, the trisulfide behaved like a glass, becoming more and more viscous, until solidification took place. No definite melting point was noted. The quartz tube containing the trisulfide was removed from the freezing mixture and allowed to warm up slowly. The thermometer remained constant for about a minute at  $-52^{\circ}$  to  $-53^{\circ}$ . This is the melting point of the trisulfide as given by Bloch and Höhn.

The hydrogen trisulfide distilled readily in the vacuum apparatus, with little or no foaming. In one case 100 cc. of the trisulfide was distilled and not more than 10 cc. of the sulfur and persulfide residue was left behind in the distilling flask. About 15 cc. of the disulfide was obtained at the same time.

Attempts were made to distil the trisulfide under atmospheric pressure. A small quartz still with ground joints was available; this was fitted with a small quartz condenser. Ten cc. of the compound was placed in the distilling flask and carefully heated. The whole mass foamed, evolving hydrogen sulfide, and leaving behind a thick gummy solution of sulfur in persulfide. One or two drops of distillate were obtained, but it was never possible to obtain a sample of sufficient size for analysis.

**Hydrogen Disulfide.**—In the second container, cooled with a mixture of carbon dioxide snow and ether, a compound of the approximate composition H<sub>2</sub>S<sub>2</sub> collected. The compound obtained never showed by analysis



the composition  $\text{H}_2\text{S}_2$ , being always 1 or 2% low in hydrogen sulfide content. The following is a typical analysis.

	1.	2.
Sample, g.....	3.4490	3.2283
Sulfur residue, g.....	1.7340	1.6220
$\text{H}_2\text{S}$ , g.....	1.7150	1.6063
% $\text{H}_2\text{S}$ .....	49.72	49.76
$\text{H}_2\text{S}$ calc. in $\text{H}_2\text{S}_2$ %.....	.....	51.20

These results indicated that the disulfide contained some dissolved trisulfide. This led to an attempt to distil the sample, obtained in the vacuum distillation, at ordinary pressures. The small quartz still, previously employed for the attempted distillation of the trisulfide, was used. Some of the disulfide was placed in the still, which was heated carefully with a micro burner. The disulfide distilled without foaming or bubbling, and was readily condensed in the small condenser which was kept at a temperature of about  $15^\circ$  by running water. The disulfide did not all distil, about  $\frac{1}{6}$  of the original volume remained behind as a gummy viscous mass. Samples of the distillate were collected directly in the quartz weighing tube and analyzed immediately. The following results were obtained.

	1.	2.
Sample, g.....	1.9172	2.0351
Sulfur residue, g.....	0.9404	0.9981
Hydrogen sulfide, g.....	0.9768	1.0370
Sulfur in sample, %.....	50.94	50.95
Hydrogen sulfide, in $\text{H}_2\text{S}_2$ , %.....	.....	51.20

The hydrogen disulfide was a practically colorless mobile oil with a much more severe and irritating odor than the trisulfide. When the disulfide was being distilled under atmospheric pressure the vapors were extremely irritating, causing tears and a smarting sensation in the nostrils. The disulfide dissolved in the same solvents as the trisulfide; it was, however, much more sensitive to small amounts of impurity than the latter. This was especially noticeable when acetone was added to the carbon disulfide solution in the analytical procedure. It was consequently necessary to be very cautious in adding the acetone in order not to have the hydrogen sulfide evolved so rapidly that the liquid would bubble over.

The boiling point of the disulfide was determined by placing some of the distilled product in a small quartz tube equipped with a two-holed rubber stopper carrying a sensitive thermometer. On gently heating, the disulfide boiled at  $74.5^\circ$ , checking the value obtained by Bloch and Höhn.

The melting point of the disulfide was determined by a method similar to the one used for the trisulfide; the cooling agent used was liquid air. The slowing up in the rise of the toluene thermometer used came at  $-88^\circ$  to  $-90^\circ$  in several trials. The disulfide behaved like the trisulfide on cooling, showing no sharp solidification point.

**Action of Trisulfide Solutions on Inorganic Salt Solutions.**—Because of the extreme ease of decomposition of the disulfide, the trisulfide was used in the experimental work which follows. The action of an ether solution of the trisulfide on solutions of various inorganic salts dissolved in the same solvent was tested. As a check on the experiments, similar solutions of the salts were treated with a saturated ether solution of hydrogen sulfide. Copper oleate gave a red-brown colloidal precipitate; ferric chloride solution gave a white precipitate, which redissolved; stannic iodide gave a buff precipitate; silver nitrate gave no change; mercuric bromide gave a yellow precipitate. In every case the saturated ether solution of hydrogen sulfide gave a similar result. It was concluded that the behavior of the trisulfide in ether solution is essentially the same as that of hydrogen sulfide.

**Action of the Trisulfide on Metallic Oxides and Oxidizing Agents.**—The effect of adding small amounts of the trisulfide to a number of metallic oxides was observed by pouring some of the trisulfide upon a small amount of the oxide placed on a carefully cleaned watch glass.

Silver oxide, copper oxide, lead peroxide and mercuric oxide caused violent decomposition of the trisulfide; the heat evolved was sufficient to ignite the persulfide.

Lead oxide, stannic oxide and magnetite brought about a violent decomposition of the trisulfide.

Arsenious oxide, arsenic oxide, ferric oxide, zinc oxide, barium peroxide and manganese dioxide caused only a slow decomposition.

The oxidizing agents potassium permanganate and potassium dichromate were found to decompose the trisulfide rapidly. The permanganate generated sufficient heat to ignite the persulfide.

**Action of the Trisulfide on Inorganic Salts.**—A number of salts were treated with small amounts of the trisulfide. The sulfates of ferrous iron, aluminum, nickel, zinc and manganese gave a very slow decomposition of the trisulfide. Anhydrous copper sulfate, however, decomposed the trisulfide rapidly, the whole mixture turning dark.

The nitrate of aluminum gave only a slow decomposition while the nitrates of lead, silver and copper caused a rapid decomposition of the persulfide. Ferric nitrate behaved in a peculiar manner; for a time no visible decomposition took place and then suddenly an increasingly violent reaction began, as if it were an autocatalytic effect.

The chlorides of manganese, sodium, cadmium, ammonium and lead decomposed the trisulfide only slowly. The chloride of antimony dissolved with the consequent decomposition of the trisulfide. The chlorides of copper and lead turned dark with accompanying decomposition of the trisulfide.

The acetate, bromide and oleate of copper decomposed the trisulfide

rapidly turning dark at the same time. Antimony tri-iodide dissolved in the persulfide. The mixture turned red and decomposed.

Massive metals did not decompose the persulfide rapidly. They became coated with the sulfide of the metal and the reaction ceased. Powdered arsenic, antimony and zinc and iron, however, brought about rapid decomposition.

It was found that the persulfide was not decomposed by finely ground quartz which had been washed with hydrochloric acid and carefully dried. Neither did boric oxide nor phosphorus pentoxide bring about decomposition. It is to be noted that all copper salts decompose the persulfide as do most lead salts.

In order to see whether it would not be possible to dissolve some of the sulfides of copper and arsenic in the pure hydrogen trisulfide and thus obtain the free sulfo acids of these metals, a small amount of freshly precipitated, well washed and dried copper sulfide was added to the trisulfide contained in a quartz tube. The sulfide did not dissolve in the persulfide and was filtered off. A similar result was obtained with fresh arsenic trisulfide.

**The Decomposition of Hydrogen Trisulfide in a Sealed Tube.**—To observe the behavior of the trisulfide under pressure, some of it was sealed in a thick glass tube which had been scrupulously cleaned and carefully dried with hydrogen chloride. The hydrogen sulfide content of the sample was 34.4%. The sealed tube was allowed to stand in a hood under ordinary laboratory conditions. At the end of 3 days small crystals of sulfur began to appear, while at the end of 5 days there were two liquid layers noticeable, the one heavy and viscous, the other light, mobile and colorless, presumably hydrogen sulfide. There were large crystals of sulfur in the tube. After 2 days more, the viscous layer had completely disappeared and the tube contained only several large rhombic crystals of sulfur and liquid hydrogen sulfide, with possibly dissolved persulfide.

**Solubility of Hydrogen Trisulfide in Hydrogen Sulfide.**—Bruni and Borgo state that hydrogen sulfide is insoluble in the persulfides. They claimed to have liquefied hydrogen sulfide and found that the persulfide did not dissolve therein. In order to establish this fact definitely, hydrogen trisulfide ( $\text{H}_2\text{S}$  content 34.4%) was carefully introduced into a clean, heavy-walled tube. The tube was placed in a freezing mixture of carbon dioxide snow and ether. By passing a current of hydrogen sulfide into the cooled tube, the gas could be easily liquefied. About two volumes of the liquid hydrogen sulfide was collected above the trisulfide and the tube was sealed off. As soon as the trisulfide melted it completely dissolved in the hydrogen sulfide. On warming to room temperature, the solution was a pale straw color. When the tube stood for 5 days large crystals of rhombic sulfur separated, but there was no separation at any time of the persulfide such as was noted in the previous case when hydrogen

trisulfide alone was sealed off. Bruni and Borgo never obtained hydrogen trisulfide, so possibly, working with persulfides containing much dissolved sulfur, the liquid hydrogen sulfide might not dissolve the compounds completely. The previously noted fact that the trisulfide alone gave a layer of liquid hydrogen sulfide and also a layer of the persulfide containing dissolved sulfur, would point to this explanation as being the correct one for Bruni and Borgo's results.

**Solubility of Sulfur in Hydrogen Trisulfide.**—To determine the amount of sulfur which would dissolve in the trisulfide, several samples of trisulfide were saturated with sulfur and the hydrogen sulfide content of the solution obtained. Sulfur dissolved until the hydrogen sulfide content of the system was between 8 and 9%. The temperature of the samples varied between 17° and 20°. Calculated on the basis that all the hydrogen sulfide was present as the trisulfide one mole of the trisulfide dissolved 8 moles of sulfur.

### Summary.

1. The conditions under which pure hydrogen disulfide and hydrogen trisulfide may be prepared in quantity have been determined.
2. A new method for analyzing the persulfides of hydrogen has been devised. This method is rapid and accurate.
3. The hydrogen persulfides decompose most slowly when stored in quartz vessels.
4. The persulfides of hydrogen are decomposed catalytically by many substances, both inorganic and organic. Of the latter, ketones, aldehydes, alcohols, amino substitution products and nitro derivatives are specially effective.
5. It has been shown that hydrogen trisulfide and liquid hydrogen sulfide are miscible, thus disproving the statement of Bruni and Borgo to the contrary.
6. Hydrogen disulfide freezes at a temperature between  $-88^{\circ}$  and  $-90^{\circ}$ .

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA.]

## A SEPARATION OF GERMANIUM AND ARSENIC.

By JOHN H. MÜLLER.

Received October 3, 1921.

In a recent publication on the atomic weight of germanium,<sup>1</sup> the author has called attention to the difficulties experienced in removing the last traces of arsenic from germanium. The distillation process from aqueous hydrochloric acid in the presence of chlorine which has been recommended did not give sufficiently accurate results as the distillate was at no time free from small quantities of arsenic.

Careful regulation of the temperature and maintenance of a low concentration of hydrochloric acid will give a distillate almost free from arsenic, but under these conditions the volatilization of the germanium is very slow or incomplete.

As the distillation from hydrochloric acid completely separates germanium from all metals and semi-metals other than arsenic, the complete removal of the latter element is all that is needed for the accurate analysis of germanium-bearing material.

A study of the relative physiological action of the derivatives of arsenic and germanium made necessary the detection and separation of small quantities of arsenic in the presence of large quantities of germanium.

Germanium dioxide was found to be non-toxic, and solutions of the same substance, when introduced subcutaneously, show a marked erythropoietic action.<sup>2</sup> It may be of interest to note that the peculiar likeness of germanium to arsenic, especially the solubility of the dioxide, suggested the study of its physiological action and that its non-toxicity links it with the non-poisonous oxides in its periodic group. In working up some 300 g. of impure germanium dioxide a separation of these closely associated elements has been found possible through a difference in their behavior toward hydrogen sulfide in presence of hydrofluoric acid.

The purpose of this paper is to describe this method.

### Experimental.

The germanium dioxide employed was some of the material used in the recent determination of the atomic weight of germanium. It was necessarily free from arsenic and other impurities

Approximately 5 g. of germanium dioxide was fused in platinum with sufficient sodium carbonate to form the normal sodium salt, the melt was dissolved in water, made up to 1 liter and the exact concentration of the solution determined by taking the mean of three analyses of 50cc.

<sup>1</sup> Müller, *THIS JOURNAL*, 43, 1085 (1921).

<sup>2</sup> Details to appear in *J. Exp. Med.*, 35, Feb. (1922).

samples. One liter of this solution contained 4.9640 g. of the dioxide. Dilution of this solution (A) to 0.1 and 0.01 concentration gave Solutions B and C respectively.

The arsenic trioxide was prepared by fractionation and resublimation of the nearly pure oxide. The standard arsenic trioxide solution was prepared like that for germanium and the concentration determined by three determinations of the trioxide as magnesium pyro-arsenate. One liter of this solution contained 4.8506 g. of arsenic trioxide. Dilution of this solution (A) to 0.1 and 0.01 concentration gave Solutions B and C respectively.

Definite portions of these solutions, in quantities shown in the table, were introduced by pipet into platinum dishes and after addition of hydrofluoric acid the solutions were saturated with hydrogen sulfide.

The hydrofluoric acid used was carefully examined and found free from iron, arsenic, silica and all metals precipitated by hydrogen sulfide.

The precipitated sulfide of arsenic was in each case filtered through filter paper in a platinum funnel upon which the sulfide was washed, first with hydrofluoric acid saturated with hydrogen sulfide and then with pure water until the washings were approximately neutral. The sulfide was then removed from the paper by dil. ammonium hydroxide and the solution evaporated in quartz. Pure conc. nitric acid was added and after evaporation of the excess of acid the arsenic was determined in the usual manner as magnesium pyro-arsenate. Porcelain Gooch crucibles with asbestos mats were employed. The acid filtrates containing the germanium, which were collected in platinum dishes, were treated with 10 cc. of pure conc. sulfuric acid and evaporated upon water-baths until nearly all of the hydrofluoric acid was expelled. The residual acid was then more strongly heated until the fuming of the residual sulfuric acid just began. When much germanium was present the dioxide tended to separate in an adherent layer on the bottom of the dish, but after diluting with water and making alkaline with ammonium hydroxide the whole was easily transferred to a glass vessel. The solution was then neutralized by addition of hydrochloric acid and sufficient excess of concentrated acid added to bring the concentration of free acid to 15–20% by weight. Hydrogen sulfide passed through this solution gave all the germanium as sulfide.

Care was taken, of course, to wash the germanium sulfide with strongly acidulated wash-water which had been thoroughly saturated with hydrogen sulfide, finishing the washing with very little cold water saturated under pressure with the same gas. The germanium was weighed as dioxide. Frequent treatment of the slowly ignited sulfide with pure nitric acid and subsequent evaporation and ignition were carried out to constant weight.

In several preliminary experiments the delicacy of the reaction of hydrogen sulfide upon hydrofluoric acid solution of arsenic trioxide was determined. It was found that as little as 0.0002 g. of arsenious oxide will be deposited as a visible precipitate from a solution containing 100 cc. of water and 50 cc. of 48% hydrofluoric acid and that this reaction may best be carried out in the cold.

A blank experiment was made with a solution containing 10 g. of germanium dioxide converted to fluoride in the presence of the 2NaF equivalent and 50 cc. of hydrofluoric acid and 300 cc. of water. Hydrogen sulfide had no effect upon this solution. The introduction of less than 0.001 g. of arsenic trioxide into a similar germanium solution gave all of the arsenic as sulfide after saturation with hydrogen sulfide. It was therefore concluded that the delicacy of this reaction for arsenic is not measurably influenced by large quantities of germanium fluoride, fluogermanic acid or the alkali salts of the latter.

The following table shows the results of eight analyses of mixtures of the oxides of germanium and arsenic. Numbers 8 and 9 are especially significant insofar as they show the possibility of separating 0.02 to 0.01% of arsenic from germanium compounds.

TABLE I.  
SEPARATION OF GERMANIUM AND ARSENIC.

Analysis.	Germanium dioxide present. G.	Arsenic trioxide present. G.	Germanium dioxide found. G.	Arsenic trioxide found. G.	Conc. hydrofluoric acid in solution (48%). Cc.	Total volume of solution. Cc.
1	0.2482	0.2425	0.2479	0.2420	50	150
2	0.2482	0.0243	0.2483	0.0234	50	100
3	0.2482	0.0024	0.2484	0.0040	50	150
4	0.2482	0.0005	0.2487	0.0004	30	110
5	0.0049	0.4851	0.0057	0.4841	55	160
6	0.0010	0.4851	0.0011	0.4839	51	152
7	10.0006	0.0020	not determined	0.0017	50	350
8	10.0002	0.0010	not determined	0.0010	50	150

### Summary and Conclusion.

1. Hydrogen sulfide is without action upon solutions of fluogermanic acid and the alkali salts of this acid.

2. Arsenic and germanium can be quantitatively separated by the action of hydrogen sulfide upon a solution of their oxides in the presence of a large excess of hydrofluoric acid.

3. The separation is sufficiently accurate to determine as little as 0.01% of arsenic in germanium compounds.

4. The method is especially useful in connection with the preparation of pure germanium compounds, as the fractional crystallization of the

double fluoride can thus be avoided and the operation carried out in small volume. The precipitation of the arsenic sulfide is complete and rapid in the cold.

PHILADELPHIA, PENNSYLVANIA.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

## THE CO-PRECIPITATION OF VANADIC ACID WITH AMMONIUM PHOSPHOMOLYBDATE.<sup>1</sup>

By J. R. CAIN AND J. C. HOSTETTER.<sup>2</sup>

Received October 6, 1921.

### 1. Introduction.

In 1912 there was developed in this laboratory a method for the determination of vanadium in which this element was separated from other materials by co-precipitation with ammonium phosphomolybdate. In the paper<sup>3</sup> describing this method no details of the mechanism of this reaction were given. The purpose of the present paper is to discuss an investigation of the mechanism of the co-precipitation of vanadic acid with the ammonium phosphomolybdate in order to define better the conditions upon which the success of the procedure as an analytical method depends and, incidentally, to throw light upon the formation of vanadophosphomolybdates and to indicate that a simple relation exists among the many members of this class of so-called "complexes."

The method, as published, is in brief outline as follows. The hot nitric acid solution containing the vanadium as vanadic acid is nearly neutralized with ammonium hydroxide, and phosphorus (as sodium phosphate) is added in an amount at least ten times that of the vanadium suspected to be present. The phosphorus is then precipitated as ammonium phosphomolybdate and the resulting precipitate is washed with ammonium hydrogen sulfate solution. Finally, the vanadium is determined by dissolving the precipitate in conc. sulfuric acid, reducing with hydrogen peroxide, and titrating with permanganate. Except for the changes of conditions made necessary in order to study the problem advantageously, this general method was adhered to in all the experiments that follow.

### 2. Preliminary Study.

It was mentioned in the former paper that the color of the ammonium

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

<sup>2</sup> The experimental work reported in this paper was carried out in 1912. Publication of the results has been delayed on account of the resignation of the authors since that time.

<sup>3</sup> "A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., based on its Quantitative Inclusion by the Phosphomolybdate Precipitate." *Bur. Standards, Tech. Paper, 8.* J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, **4**, 250 (1912).



phosphomolybdate containing vanadium varies with the ratio of phosphomolybdate to vanadic acid (or, more conveniently expressed, of phosphorus to vanadium) at the time of precipitation. With small amounts of phosphorus and large amounts of vanadium the color of the resulting precipitate is deep orange or even dark red, while with greater quantities of phosphorus (with the same amount of vanadium) the precipitate approaches yellow as the limiting color. It was at first thought that this lighter color was due merely to a mixture of an ammonium vanado-phosphomolybdate with pure ammonium phosphomolybdate and, accordingly, experiments were made in order to determine which one of the numerous vanado-phosphomolybdates was present. This preliminary test consisted of a precipitation of the same quantities of phosphomolybdate in the presence of varied amounts of ammonium vanadate. If but one ammonium vanado-phosphomolybdate were formed under these conditions the precipitates formed from all solutions containing more than the required amount of vanadium would have the same color. Instead of possessing one color, however, the successive precipitates showed a progressive change from the very light orange of the one formed in the presence of little vanadium to the deep orange of that containing most vanadium. This made it evident that the resulting precipitate is not of constant composition, *i. e.*, it is not a chemical compound as the term is commonly used. Because of the indication afforded by this preliminary test it was decided to study the phenomenon quantitatively.

### 3. Quantitative Study.

#### A. Reagents.

The following solutions were prepared.

**Sodium Phosphate Solution.**—This was made up to contain about 124 g. of sodium phosphate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , per liter of solution. It was standardized (1) by evaporating known volumes to dryness and igniting the residue to sodium pyrophosphate,  $\text{Na}_4\text{P}_2\text{O}_7$ , and (2) by precipitating as ammonium magnesium phosphate, and weighing finally as magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ . The value of 1 cc. of the solution was found to be by (1), 11.53 and by (2), 11.52 mg. of phosphorus.

**Ammonium Metavanadate Solution** was so prepared that 1 cc. was approximately equal to 0.5 mg. of vanadium. This solution was frequently standardized by titration with permanganate after reduction with hydrogen sulfide, sulfur dioxide, or hydrogen peroxide.<sup>4</sup>

**Potassium Permanganate Solution** was 0.01 *N*, and was standardized against sodium oxalate.

**Molybdate Reagent** was made up according to Blair.<sup>5</sup>

**Ammonium Molybdate Solution** contained 60 g. of the salt per liter.

<sup>4</sup> "The Reduction of Vanadic Acid in Concentrated Sulfuric Acid Solution by Hydrogen Peroxide and by Persulfates." J. R. Cain and J. C. Hostetter, *THIS JOURNAL*, 34, 274 (1912).

<sup>5</sup> Blair, "The Chemical Analysis of Iron," 8th ed., p. 92.

### B. The Ratio of Vanadium to Phosphorus in the Solid Phase.

**Series One. Vanadium Constant, Phosphorus Varied.**—A study of the ratio of phosphorus to vanadium in the solid phases, when constant amounts of vanadium and varied amounts of phosphorus are present, was carried out as follows. Equal volumes of the ammonium vanadate solution were measured into flasks; ammonium nitrate in definite amounts and sodium phosphate solution in gradually increased quantities were then added to the contents of the successive flasks. The different solutions were made up to equal volumes with water and then, after adjusting the temperature, the phosphorus was precipitated by molybdate reagent. The temperature of the phosphorus-vanadium solution could easily be adjusted so that after the addition of molybdate reagent the final temperature was approximately 65°. The phosphomolybdate was allowed to settle out and the amount of vanadium which was carried down was determined, as mentioned above, by reducing with hydrogen peroxide and titrating with permanganate. Other details are given in the tables.

TABLE I.  
PRECIPITATION OF VANADIUM. VANADIUM CONSTANT; PHOSPHORUS VARIED.  
Temp., 65°. 5 g. of Ammonium Nitrate Used in All Experiments.

Vanadium present. Mg.	Total volume. Cc.	Phosphorus added. Mg.	Vanadium pptd. Mg.	Phosphorus added. Mg.	Vanadium pptd. Mg.
With 50 g. of Molybdate Reagent.				20.1 mg. of Vanadium present; 100 cc. of Molybdate reagent; 190 cc. Total Volume.	
4.66	108.7	2.30	1.40	5.18	6.18
		4.60	2.41	5.76	6.01
		9.21	3.47	11.52	10.2
		11.52	3.82	17.26	10.2
		17.28	4.32	23.04	14.5
		23.04	4.70	28.8	15.0
		34.56	4.63	34.6	16.6
		40.32	4.72	40.3	16.4
		2.30	2.96	46.1	17.8
		5.76	4.97	51.9	17.8
10.05	120	11.52	7.23	57.6	19.5
		17.28	8.53	63.3	19.3
		23.04	9.24	69.0	19.8
		With 100 g. of Molybdate Reagent.			
10.05	170	25.31	9.05	74.8	19.1
		28.80	9.32	80.6	18.6
		31.10	9.24	92.1	19.3
		34.56	9.54	97.9	19.9
		36.90	9.39	103.7	18.8
		40.32	9.70	115.2	20.5
		42.7	9.44	161.3	20.8
		46.1	9.87		
		51.9	10.2		
		69.1	10.2		

After completing a series in this manner other series were run similarly but with different initial amounts of vanadium. The data so obtained are given in Table I, and shown graphically in Fig. 1.

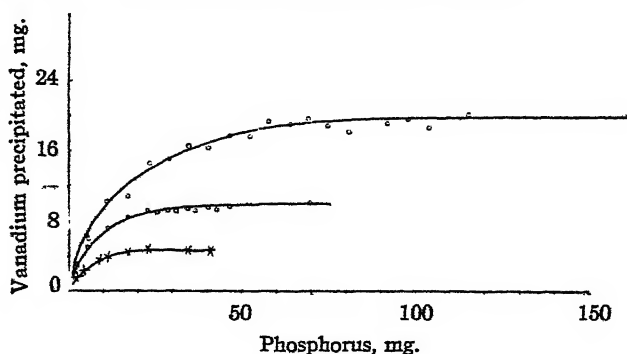


Fig. 1.

Inspection of these curves shows that under the conditions that obtain here complete precipitation is brought about by an amount of phosphorus approximately 5 times that of the vanadium. This ratio of 5:1 is only half of that which was used in the investigation described in the first paper, but the larger excess was thought to be necessary in order to insure complete precipitation under the somewhat different conditions there employed. An excess of precipitant seems to eliminate irregularities in the amount of vanadium precipitated, which sometimes occur under different conditions of temperature, acidity and especially of agitation during the actual precipitation. Thus, shaking the precipitating solution on a mechanical shaker causes less co-precipitation of vanadium than when the reagents are merely mixed and the precipitate is allowed to form and settle. This, however, is true only when the amount of phosphorus is far too low for complete precipitation. Since, in the series that follow, the amount of phosphorus was always less than that required for complete precipitation, the precipitates were allowed to settle on standing rather than shaken out on a machine.

The curves of Series 1 follow, within the experimental error, the equation  $V/P = BC^m$ , in which  $V/P$  is the ratio of vanadium to phosphorus in the solid phase,  $C$  the concentration of vanadium remaining in the solution, and  $B$  and  $m$  are constants. Expressing  $C$  in mg. of vanadium in 100 cc. of solution, the equation is  $V/P = 0.38 C^{0.47}$ . Further discussion of these curves and of the above equation will be taken up later.

**Series Two. Phosphorus Constant, Vanadium Varied.**—In this series, equal amounts of phosphorus were precipitated in the presence of gradually increasing quantities of vanadium. The same conditions of precipitation obtain here as for Series One except that with the higher vana-

dium concentrations the flask was shaken until an actual separation of the solid phase took place, after which the rest of the precipitate separated on long standing.

The results obtained are given in Table II and shown in Fig. 2. A comparison of the curve with the curves of Series 1 shows that they are very similar in general character.

TABLE II.

PRECIPITATION OF VANADIUM. PHOSPHORUS CONSTANT; VANADIUM VARIED.

23.4 mg. of Phosphorus, 20 g. of Ammonium Nitrate, 50 cc. of Molybdate Reagent and Total Volume of 250 cc. in All Experiments. Room Temperature.

Total vanadium. Mg.	Vanadium pptd. Mg.
4.66	4.70
10.0	9.24
20.0	15.1
25.0	19.1
50.0	29.0
100	35.3
150	41.3
200	42.0

Closer study, however, reveals the fact that when the ratio of vanadium to phosphorus becomes very high the curve of Series 2 does not rise as

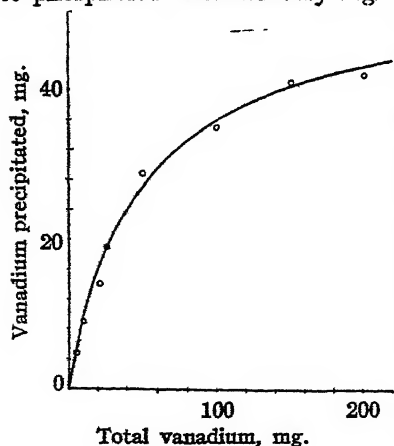


Fig. 2.

rapidly as would be expected. This is in accord with the well-known fact that ammonium phosphomolybdate is not precipitated at all in the presence of an exceedingly high concentration of vanadic acid. This unfortunate condition makes it impossible to extend the curve further, and hence limits the application of this method as applied to the preparation of ammonium vanado-phosphomolybdates.

It is essential to note that the color of the precipitates secured along this curve varies gradually from a light orange to a very dark orange.

This increase in color is continuous and is likewise parallel to the increasing vanadium content. Another interesting fact is that the color of the highest member of this series is very nearly that of the lowest member of a series of ammonium vanado-phosphomolybdates prepared in another manner by William Blum,<sup>6</sup> specimens of which he has very kindly placed at our disposal. In color, Blum's series ran through combinations

<sup>6</sup> Blum, *THIS JOURNAL*, 30, 1860 (1908).

of orange, red, and brown up to the highest member, which was black. Combining these two series we have then a perfect continuity in the colors possessed by the numerous ammonium vanado-phosphomolybdates. At one end of the complete series is ammonium phosphomolybdate with the ratio of vanadium to phosphorus equal to zero and at the other end ammonium phosphovanadate with this ratio relatively large. Extending from ammonium phosphomolybdate toward the other limiting compound there is probably a series of *solid solutions*, in which the relative quantities

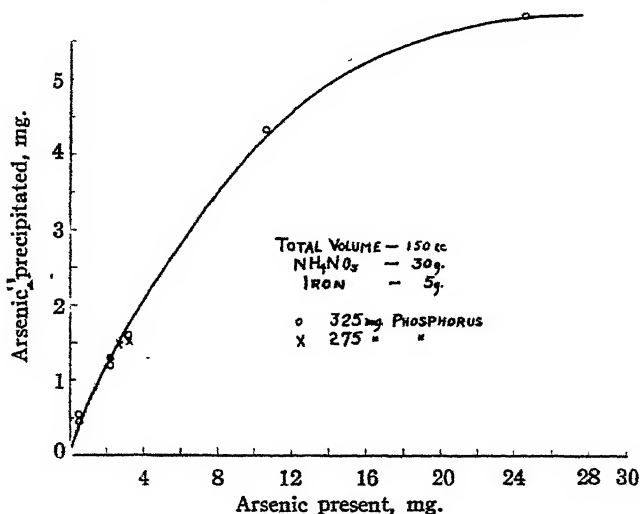


Fig. 3.

of the components can vary continuously within certain limits. This point will be referred to later.

**The Co-precipitation of Arsenic with Ammonium Phosphomolybdate.**—For purposes of comparison we may here insert an account of an investigation by Frank and Hinrichsen<sup>7</sup> on the co-precipitation of arsenic with ammonium phosphomolybdate. The similarity between their results for arsenic and ours for vanadium is very striking. Their most complete series of experiments corresponds to that just described, namely, precipitation of arsenic with fixed concentration of phosphorus. Their results, plotted in Fig. 3, are quite comparable with those for vanadium plotted in Fig. 2. It is evident that the mechanism of the reaction in the case of arsenic is the same as that for vanadium.

**Series Three. Effect of Dilution.**—In this series the only condition that was varied was the concentration of the reacting substances at the time of precipitation. The total volume of the system was increased by steps from about 100 cc. to 1000 cc. The data are given in Table III and plotted in Fig. 4.

<sup>7</sup> Frank and Hinrichsen, *Stahl u. Eisen*, 28, 295 (1908).

TABLE III.

PRECIPITATION OF VANADIUM. EFFECT OF DILUTION AND OF AMMONIUM NITRATE CONCENTRATION.

Temp., 85°. 10.05 mg. of Vanadium, 23.04 mg. of Phosphorus, and 50 cc. of Molybdate. Reagents Used in All Experiments.

Ammonium nitrate. G.	Total volume. Cc.	Vanadium pptd. Mg.
5.0	108	9.24
	170	8.20
	200	6.42
	400	4.40
	600	3.09
	800	2.23
	1000	1.71
100.0	1000	8.94

*Effect of Ammonium Nitrate.*—In connection with the results obtained upon the effect of dilution on the amount of vanadium carried down it

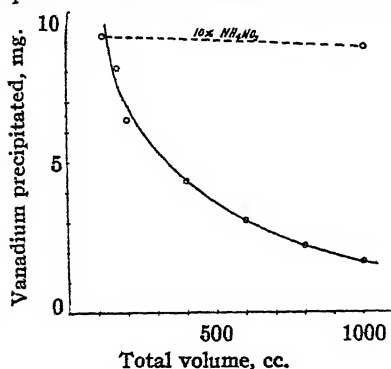


Fig. 4.

was suspected that ammonium nitrate was an essential factor in the co-precipitation. Accordingly, the precipitation of the most highly diluted system (1000 cc. in volume) was repeated with the addition of 100 g. of solid ammonium nitrate. The result was, within the experimental error, identical with that obtained when the total volume was but 100 cc. This confirmed what had been empirically established before, that ammonium nitrate counteracts the influence of dilution on the co-precipitation of the vanadic acid. The theoretical significance of this will be discussed later.

An identical effect with ammonium nitrate was observed by Frank and Hinrichsen on the co-precipitation of arsenic by ammonium phosphomolybdate. In their experiments they used 20 or 30 g. of nitrate in 150 cc. and found that the co-precipitation of arsenic was favored by the addition of this salt.

**Series Four. Effect of Temperature.**—The results given in Table IV show that the maximum co-precipitation occurs within the range 40°–50°. The exact curve (Fig. 5) is difficult to reproduce but each set of

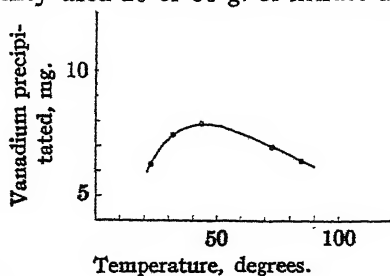


Fig. 5.

results exhibited a maximum in this region. These results are in partial accord with those of Brearley and Ibbotson<sup>8</sup> who found more vanadium precipitated at the higher than at the lower temperatures. These data are not in accord with their assertion, however, that phosphomolybdates precipitated in the cold are free from vanadium, a result that is possible only under limiting conditions, as is evident from the data already presented.

TABLE IV.

## PRECIPITATION OF VANADIUM. EFFECT OF TEMPERATURE.

10.05 mg. of Vanadium; 23.0 mg. of Phosphorus; 5 g. of Ammonium Nitrate; 50 cc. of Molybdate Reagent; Total Volume, 120 cc.

Temp. °C.	Vanadium pptd. Mg.
23	6.23
32	7.43
44	7.88
74	6.92
85	6.45

**Series Five. Effect of Acidity.**—The effect of acidity on the co-precipitation was studied by adding standardized nitric acid in gradually increased volumes to a succession of mixtures of otherwise neutral solutions of sodium phosphate, ammonium vanadate and nitrate. The precipitant was an ammonium molybdate solution prepared from the crystallized salt. The data given in Table V and presented graphically in Fig. 6

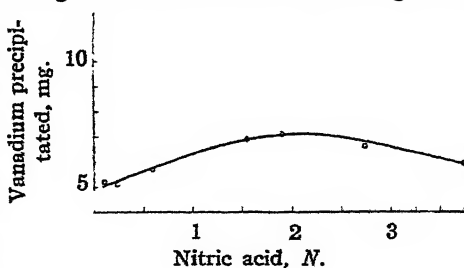


Fig. 6.

show that the maximum co-precipitation takes place in a nitric acid concentration of approximately 2 N. In practice this concentration is

TABLE V.  
EFFECT OF ACIDITY.

10.05 mg. of Vanadium; 23 mg. of Phosphorus; 2.5 g. of Molybdic Acid; 5 g. of Ammonium Nitrate; Total Volume, 170 cc. Temp., 65°.

Nitric acid. N.	Vanadium pptd. Mg.
0.12	5.2
0.24	5.1
0.60	5.7
1.55	6.9
1.90	7.1
2.73	6.6
3.75	5.9

<sup>8</sup> Brearley and Ibbotson, "The Analysis of Steel-works Materials," 1902, pp. 164-166.

roughly secured by adding to the nearly neutral solution, containing the vanadium and phosphorus, an equal volume of the molybdate reagent as ordinarily made.

#### 4. Discussion of Results.

A study of the curves in Series 1, 2 and 3 clearly indicates that (1) the curve showing the relation of phosphorus to vanadium in the solid phase is *logarithmic* and not linear as would be expected if the precipitate were a chemical compound; (2) with a given amount of phosphorus the amount of vanadium in the precipitate depends upon the *concentration of vanadium* initially present. The co-precipitation of the phosphorus and vanadium might be referred to as (1) an occlusion, (2) an absorption, (3) an adsorption, or (4) a partition effect. Without attempting to decide which term best describes the known facts, we shall merely call attention to the well-known fact that when any substance distributes itself between two solvents X and Y, the concentrations of the dissolved substance in the two solvents being  $C_x$  and  $C_y$  respectively and the molecular weight of the dissolved substance in the solvent X being 20 times the molecular weight in the solvent Y, then the ratio  $C_x/C_y^n$  is constant. Now, as shown above, the equation  $V/P = 0.38 C^{0.47}$  satisfactorily represents the curves of Series 1. In this equation  $C$  is the concentration of vanadium remaining in the solution, and if the precipitate be thought of as a *solid solution* of the vanadium compound in the phosphorus compound,  $V/P$  is for practical purposes the concentration of vanadium in the solid solution. That is,  $C_x/C_y^{0.47} = 0.38$ , and therefore the phenomena with which we are dealing may be described as a case of the distribution or partition of a solute (the vanadium compound) between two solvents one of which is a liquid and the other a solid. The exponent 0.47 is nearly equal to  $1/2$  and hence the molecular weight of the compound when dissolved in X (*i. e.*, in solid solution) would be half as great as its molecular weight in Y (*i. e.*, in aqueous solution). Whether or not this viewpoint is the correct one can be determined only by further experimentation, but for convenience we shall refer to the phenomena as a partition effect.

Inasmuch as we are dealing then with a partition effect it is evident that the precipitation of vanadic acid by ammonium phosphomolybdate is never complete. However, we can make the residual quantity just as small as we like by a process analogous to that of extraction with immiscible solvents. If the amount of vanadium is small we can secure all but the merest trace by making the quantity of precipitant sufficiently great. When the vanadium content is high, more thorough separation is obtained by precipitating several times with smaller portions of phosphomolybdate. If conditions are carefully adjusted and the ratio of phosphorus to vanadium is at least 10, only negligible traces of vanadium will remain in the solution when precipitating from 1 to 10 mg. of this element.



The effect of ammonium nitrate upon the partition—increasing the amount of vanadic acid carried down—may perhaps be a consequence of a repressing effect upon the dissociation of the vanadium complex co-precipitated. This would be in exact accord with what has been shown by Richards on the occlusion of ferric sulfate by barium sulfate;<sup>9</sup> by Richards, McClaffrey, and Bisbee, on the occlusion of magnesium oxalate by calcium oxalate;<sup>10</sup> and by Baxter on the occlusion of molybdic acid and ammonium molybdate by ammonium phosphomolybdate,<sup>11</sup>—namely, that co-precipitation in these cases is the distribution of an undissociated substance between the solution and the nascent solid. Any condition, therefore, which tends to decrease the concentration of the undissociated portion,—for instance, dilution,—tends to decrease the amount of this substance co-precipitated, and conversely.

**Vanado-phosphomolybdates in General.**—Taking up the subject of ammonium vanado-phosphomolybdates in general one cannot but wonder at the large number of these “compounds” that have been described. It is merely necessary to emphasize that no less than 27 of them are mentioned in Gmelin-Kraut<sup>12</sup> in addition to those (8 in number) subsequently prepared by Blum. We will note further that Toggenburg<sup>13</sup> found certain of his “compounds” underwent changes in composition when recrystallized.

It is difficult to believe that all of the combinations between these components that have been described are true chemical compounds. The large number of these “compounds” described in the literature is, in itself, a reason for considering them other than chemical compounds and suggests that they are related in some simple manner. That such a relation exists between the many members in this and in other series of salts of similar complex inorganic acids has already been suggested by Wherry.<sup>14</sup> From a study of the optical properties<sup>15</sup> of the series of vanado-phosphomolybdates prepared by Blum he concluded that “it is surely not permissible to call them chemical compounds,” and “that they are but a step removed from the so-called ‘adsorption-compounds’ of colloid-chemistry.” His conclusion is in harmony with the conclusions of this paper, since the relation between adsorption and occlusion is very close. That

<sup>9</sup> Richards, *Z. anorg. chem.*, 23, 383 (1900).

<sup>10</sup> Richards, McClaffrey and Bisbee, *Z. anorg. chem.*, 28, 71 (1901).

<sup>11</sup> Baxter, *Am. Chem. J.*, 28, 298 (1902).

<sup>12</sup> Gmelin-Kraut, “Handbuch der anorganischen Chemie,” 7th ed., III, 2, pp. 205–211.

<sup>13</sup> *Dissertation*, Bern, 1902, pp. 22 and 29.

<sup>14</sup> Wherry, *J. Franklin Inst.*, 169, 487 (1910).

<sup>15</sup> Some of the solids prepared in the course of this investigation were very kindly examined microscopically by Mr. A. A. Klein. Time was not available for the preparation of more suitable specimens, however, and accordingly the results obtained were not conclusive. The authors wish to express here their appreciation of Mr. Klein's interest in the matter.

these complex salts are indeed intimately related to "adsorption-compounds" is evident from the similarity between the equation representing the occlusion of vanadic acid and that of the "adsorption isotherm."

Having indicated, therefore, that many of the "ammonium vanado-phosphomolybdates" are probably solid solutions it is an easy task to account for their number. They may be considered as points on the curve showing the amount of vanadium occluded by a fixed amount of phosphorus in the presence of increasing amounts of vanadium. This curve is that of Series 2 and its extension. When viewed from this standpoint, one cannot but wonder that many more "compounds" have not been described, inasmuch as there is an infinite number of possible combinations.

The fact that Toggenburg found his salts to change composition on recrystallization is clearly accounted for by the partition effect already shown. It is, in fact, to be expected. If a solid separates from a solution of one of these salts it must bring about a partition of material between the solid and the solution, causing thereby a progressive change in composition of the solid. The composition of the solid phase would also depend upon the concentration of the solution (Series 3) and upon other conditions such as temperature (Series 4). Only under limiting conditions, therefore, would the solid phase be identical with that of the original salt.

### 5. Summary.

1. The co-precipitation of vanadic acid with ammonium phosphomolybdate may be explained as a phenomenon resulting from a partition of the vanadic acid in some undissociated form between the solution and the solid phase.

2. The maximum absorption by the solid phase occurs at a temperature of 40° to 50° and in a nitric acid concentration of 2 *N*.

3. The effect of dilution in lowering the amount of occlusion is a direct result of the partition law and can be minimized by the presence of ammonium nitrate, the latter probably tending to repress the dissociation of the vanadium complex which is occluded.

4. The ammonium vanado-phosphomolybdates are probably a series of solid solutions the end members of which may be ammonium phosphomolybdate and ammonium phosphovanadate; the exact relations can be established only by a thorough investigation of the appropriate systems.

Acknowledgment of helpful suggestions and criticism should here be made to Dr. William Blum of the Bureau of Standards and to Dr. L. H. Adams of the Geophysical Laboratory.

WASHINGTON, D. C.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 137.]

## THE POTENTIALS AT THE JUNCTIONS OF MONOVALENT CHLORIDE SOLUTIONS.

BY DUNCAN A. MACINNES AND YU LIANG YEH.

Received October 8, 1921.

### 1. Introductory.

The importance of the measurement and estimation of the potentials at the junctions of salt solutions does not need to be emphasized. Many investigations involving determinations of ion activities and of the free energies of reactions are rendered difficult or uncertain because of the necessity of correcting for these troublesome points of contact. The research to be described in the following pages was made with the purpose of finding the conditions for constant and reproducible junctions and with the hope of adding to our theoretical knowledge of the subject. The investigation was restricted to an examination of junctions of the type  $MCl | M'Cl$  in which  $M$  and  $M'$  represent hydrogen or one of the alkali metals. The same electrolyte concentration was maintained on both sides of each boundary. These junctions were studied because (a) electrodes reversible to the chloride ion are easily made and are reproducible, and (b) certain simplifying assumptions regarding the chloride ion have resulted from recent work. Further, as one of the authors has shown, connection between any two solutions of univalent ions, with one ion in common, can be made by combining a junction of the type just mentioned with one in which the concentration, but not the salt, changes. The formation and computation of the potentials of the latter type of junctions is now well understood.<sup>1</sup>

A large bibliography on liquid junctions could be collected, but the following references will be sufficient for our purpose. Apparently the first experimental work in connection with the evaluation of liquid junction was carried out by Nernst.<sup>2</sup> Further studies have been made by Lewis and Sargent,<sup>3</sup> by Cumming and Gilchrist,<sup>4</sup> by Meyers and Acree,<sup>5</sup> and by Lewis, Brighton and Sebastian.<sup>6</sup> In all but one of the articles mentioned the authors point out that the potentials of junctions connecting two different salts are variable. It seems to be tacitly assumed that the highest voltage, if moderately constant, is the "correct" value.

<sup>1</sup> See MacInnes, *THIS JOURNAL*, 37, 2301 (1915); and MacInnes and Beattie, *ibid.*, 42, 1117 (1920).

<sup>2</sup> Nernst, *Z. physik. Chem.*, 4, 129 (1889).

<sup>3</sup> Lewis and Sargent, *THIS JOURNAL*, 31, 363 (1909).

<sup>4</sup> Cumming and Gilchrist, *Trans. Faraday Soc.*, 9, 174 (1913).

<sup>5</sup> Meyers and Acree, *Am. Chem. J.*, 50, 396 (1913).

<sup>6</sup> Lewis, Brighton and Sebastian, *THIS JOURNAL*, 39, 2245 (1917).

A method of renewing the surface between the two salt solutions, at intervals, is described by Lewis, Brighton, and Sebastian.<sup>6</sup> Walpole<sup>7</sup> has found that constant potentials can be obtained by forming the junctions with tapes, along which the solutions are flowed. The most decided advance, however, in the direction of the formation of reproducible potentials was made by Lamb and Larson<sup>8</sup> who used a device which produces a junction which is constantly renewed. The following investigation was made with an apparatus which in most respects resembles that of the authors just mentioned, although it was, to an extent at least, developed independently.

## 2. The Apparatus.

The apparatus used in our experiments on the more dilute solutions (0.01 *N*) is shown in Fig. 1.

The boundary which formed at A, resulted from the meeting of two slowly moving streams of solution from the reservoirs B and C. The flow was regulated by a screw pinchcock on a rubber tube attached to the tube F. An addition to the apparatus as described by Lamb and Larson is the glass rod D which is tipped with rubber. When lowered this rubber tip fits into a constriction in the tube and temporarily separates the two halves of the apparatus containing the different solutions, making it possible to fill the reservoir without mixing the liquids. Unless this device is used it is very difficult to sweep out the resulting mixed solutions in the apparatus and obtain constant potentials. The tubes between the electrodes G and H were, as far as possible,

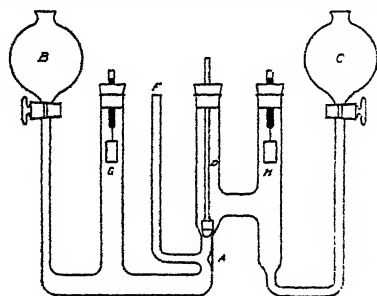


Fig. 1.

made wide, so as to cut down the resistance and increase the sensitivity of the potential measurements. A similar apparatus but made of narrower tubing was used for the experiments with 0.1 *N* solutions.

In making a measurement the procedure was as follows. The apparatus was first dried and cleaned, then the rubber tip on D was pushed into the constriction near A, and the two solutions were poured into the appropriate portions of the vessel. The electrodes G and H and stoppers were next inserted, the pinchcock on F closed, the reservoirs B and C partly filled and the stopcocks closed. The whole apparatus was then placed in a thermostat where it was rigidly supported. Adjustment was then made so that the tops of the reservoirs B and C were accurately in the same horizontal plane, after which these reservoirs were completely filled. The system was then ready for lifting of the plug D, opening the stopcocks and the pinchcock on F, after which a boundary soon formed at A and measurements of the potential

<sup>7</sup> Walpole, *J. Chem. Soc.*, 105, 2521 (1914).

<sup>8</sup> Lamb and Larson, *THIS JOURNAL*, 42, 229 (1920).

between G and H were determined with the potentiometer. It is evident that if the precaution of leveling of the tops of the two reservoirs is not observed there will be an initial surge of liquid through the apparatus and mixing of the solutions at A will result. It was found that if such mixing occurred that no amount of flowing would produce constant potentials and that the experiment had to be started, with a dry vessel, from the beginning. It was also found that for a steady flow, and to avoid entrapping air, the stopcocks should be made of large bore, (about 2.5 mm.).

The nature of the boundary between the two solutions was made clearly visible by operating the apparatus with two solutions, one of which contained a few drops of phenolphthalein and the other a small amount of sodium hydroxide, the pink color of the indicator showing only at the surface of the solutions and in the region in which they had mixed or diffused. A surface of almost microscopic thinness started at A and persisted, with a slight thickening, throughout the length of tube F. If the flow is stopped the colored area thickens at A, if too rapid there is evidence of turbulence. The depression at A (also present in Lamb and Larson's apparatus) prevented mixing due to a "dead space."

### 3. The Reversible Electrodes.

Following Lewis and Sargent<sup>9</sup> some experiments were made with gold electrodes surrounded by the salt solutions under investigation, to which definite small amounts of ferro- and ferri-cyanides were added. Our experiments with these electrodes were, however, not successful. Calomel electrodes, although carefully made, were not very satisfactory, particularly with hydrochloric acid as electrolyte.

The final experiments were all carried out with silver-silver chloride electrodes formed on a platinum gauze, as described by MacInnes and Parker,<sup>10</sup> with the additional precaution, recommended by MacInnes and Beattie,<sup>1</sup> of forming the layer of chloride in a solution of the same concentration and composition as that in which the electrodes are to be used. Such electrodes agreed with each other, when placed in the same solution, to 0.03 mv. or less.

The electromotive-force measurements were made with a Leeds and Northrup potentiometer which was calibrated during the investigation. The standard cell used was compared at intervals with a cell which had been recently standardized by the Bureau of Standards. The apparatus was placed in a thermostat which was regulated to  $25^{\circ} \pm 0.03^{\circ}$ , the latter being measured on a thermometer calibrated by the Bureau mentioned.

### 4. Preparation of Solutions.

**Hydrochloric Acid.**—The hydrochloric acid solutions were prepared by diluting

<sup>9</sup> Ref. 3, p. 355.

<sup>10</sup> MacInnes and Parker, *THIS JOURNAL*, 37, 1445 (1915).

the constant-boiling mixture prepared as directed by Hulett.<sup>11</sup> The concentration of this acid was checked by analysis.

**Sodium and Potassium Chlorides.**—The "c. p." salts furnished by a well-known manufacturer were recrystallized 5 times from conductivity water and then fused. The solutions were then prepared by weighing out the requisite amount of dry salt.

**Ammonium Chloride.**—A good commercial grade of the salt was sublimed. A concentrated solution was then prepared and analyzed, after which solutions of desired concentrations were obtained by dilution.

**Lithium Chloride.**—This salt was kindly furnished, after careful purification, by J. A. Beattie of this laboratory. Solutions were made by diluting an analyzed concentrated solution.

**Cesium Chloride.**—Cesium chloro-iodide, which was prepared from an impure cesium salt, was recrystallized several times, after which the chloride was formed by heating. A 0.01 *N* solution was made by diluting an analyzed concentrated solution.

## 5. Theoretical Discussion.

A simple derivation, (similar in a number of respects to that given by Henderson,<sup>12</sup>) of an expression for the potential at a junction of the type  $\text{HCl}|\text{KCl}$ , in which the same concentration of electrolyte exists on both sides of the boundary, is given below. It differs from that of Planck in detail and in generality, but it has the advantage of indicating clearly the nature of the necessary assumptions, which can be compared with those of the more modern theory of strong electrolytes. For the sake of concreteness the derivation will be carried out with reference to solutions of the two substances given above.

At the surface where the two solutions meet there will be a layer in which the concentrations change continuously from pure hydrochloric acid to pure potassium chloride. Let us consider an intermediate plane in this layer. If the total concentration is  $c$  and that of the hydrochloric acid at all points in this plane is  $x$  then the concentration of potassium chloride is  $c - x$ . We are assuming that the boundary is formed by mixing and that appreciable diffusion has not occurred. Points on another plane a short distance,  $dl$ , away will have concentrations of  $x + dx$ , and  $c - (x + dx)$ , respectively. Let us consider the potential difference,  $dE_1$ , between two such planes. The passage of one faraday,  $F$ , of current across these planes will be attended by the change of free energy

$$FdE_1 = RT(T_K d\ln a_K + T_H d\ln a_H - T_{Cl} d\ln a_{Cl}) \quad (1)$$

in which  $E_1$  is the liquid junction potential,  $a_K$ ,  $a_H$  and  $a_{Cl}$  are the activities of the potassium, hydrogen and chloride ions and  $T_K$ ,  $T_H$  and  $T_{Cl}$  are the transference numbers of the ions in the mixture at this particular point. In this connection some recent work by Chow<sup>13</sup> and Harned<sup>14</sup> have shown that, for moderate concentrations, we can safely assume,

<sup>11</sup> Hulett, *THIS JOURNAL*, **31**, 390 (1902).

<sup>12</sup> Henderson, *Z. physik. Chem.*, **59**, 118 (1907).

<sup>13</sup> Chow, *THIS JOURNAL*, **42**, 497 (1920).

<sup>14</sup> Harned, *ibid.*, **42**, 1808 (1920).

for potassium chloride and hydrochloric acid solutions at least, that the activity of the chloride ion is the same in both solutions and throughout the boundary, *i. e.*, that  $d \ln a_{\text{Cl}} = 0$ .

The transference numbers  $T_{\text{K}}$  and  $T_{\text{H}}$  at points on the plane referred to above will be

$$T_{\text{H}} = \frac{x/c \cdot \Lambda_{\text{H}}}{x/c \cdot \Lambda_{\text{H}} + (c-x)/c \cdot \Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \text{ and } T_{\text{K}} = \frac{(c-x)/c \cdot \Lambda_{\text{K}}}{x/c \cdot \Lambda_{\text{H}} + (c-x)/c \cdot \Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \quad (2)$$

in which  $\Lambda_{\text{H}}$ ,  $\Lambda_{\text{K}}$  and  $\Lambda_{\text{Cl}}$  are the equivalent conductances of the ions at the concentrations involved. If  $x/c = l$  and  $\frac{c-x}{c} = (1-l)$  Equations 2 become

$$T_{\text{H}} = \frac{l\Lambda_{\text{H}}}{l\Lambda_{\text{H}} + (1-l)\Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \text{ and } T_{\text{K}} = \frac{(1-l)\Lambda_{\text{K}}}{l\Lambda_{\text{H}} + (1-l)\Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \quad (3)$$

The assumption that  $\Lambda_{\text{Cl}}$  is the same on both sides of the boundary is justified by the computations of Lewis<sup>15</sup> and of MacInnes,<sup>16</sup> except for solutions whose viscosities are appreciably different. Chow<sup>13</sup> and Harned<sup>14</sup> have shown that the individual activities of the ions of hydrochloric acid and potassium chloride are the same at one concentration in solutions of the pure substances and in mixtures of the same total electrolyte concentration. Under these conditions then the ratios of the ion activities  $a_{\text{H}}$  and  $a'_{\text{H}}$  at two planes in the junction will be proportional to the corresponding concentrations  $x$  and  $x'$ , and the activities of the other positive ion will be proportional to values of  $c-x$ . (This does not involve the assumption that the activities of the hydrogen and potassium ions are equal.) We, therefore, have the relations

$$d \ln a_{\text{H}} = d \ln x/c = d \ln l = dl/l \quad (4)$$

$$d \ln a_{\text{K}} = d \ln (c-x)/c = -d \ln (1-l) = -dl/(1-l). \quad (4a)$$

Substituting 3, 4, and 4a in 1:

$$F dE_1 = RT \frac{(\Lambda_{\text{H}} - \Lambda_{\text{K}}) dl}{l(\Lambda_{\text{H}} - \Lambda_{\text{K}}) + \Lambda_{\text{K}} + \Lambda_{\text{Cl}}}. \quad (5)$$

Integrating between  $l = 0$  and  $l = 1$  we have

$$E_1 = \frac{RT}{F} \ln \frac{\Lambda_{\text{K}} + \Lambda_{\text{Cl}}}{\Lambda_{\text{H}} + \Lambda_{\text{Cl}}}. \quad (6)$$

This equation, in which the conductances refer to the concentration under consideration rather than to the limiting values, is a modification of the original Planck equation recommended by Lewis and Sargent.<sup>3</sup>

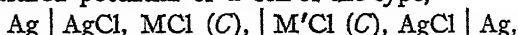
To summarize, the assumptions involved in this derivation are: (a) that the electrolyte concentration is constant throughout the boundary, *i. e.*, that the boundary is formed by mixture and not by diffusion; (b)

<sup>15</sup> Lewis, *THIS JOURNAL*, **34**, 1640 (1912).

<sup>16</sup> MacInnes, *ibid.*, **41**, 1086 (1919), and **43**, 1217 (1921).

the ion activities are independent, at each concentration, of the nature of the (monovalent) oppositely charged ions in solution; and (c) the ion conductances are also independent, at each concentration, of the accompanying ions. The validity of (b) has been tested, as already mentioned, by Chow and by Harned, for solutions of the pure substances and for mixtures; assumption (c) at moderate concentrations holds for many, if not most of the univalent salts,<sup>17</sup> and is a close approximation for such mixtures as have been investigated. (Work on the conductances of mixtures of electrolytes is in progress in this laboratory.) Assumption (a) will be discussed in the next section.

It should also be noted that if the activity of the chloride ion at any one concentration is the same in two alkali chloride solutions or in hydrochloric acid the measured potential of a cell of the type,



is the potential of the liquid junction, since equal electrode potentials oppose each other.

## 6. Experiments on Rates of Flow.

With the apparatus described in the previous sections it was, of course, important to determine the effect of the rate of flow upon the potential

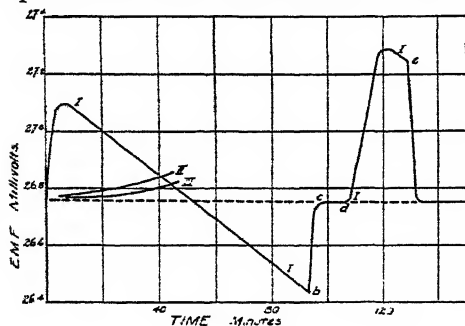


Fig. 2.

of the liquid junction. Fig. 2, in which the ordinates are potentials in millivolts and the abscissas times in minutes, summarizes, graphically, the results of the experiments on the junction between 0.1 *N* hydrochloric acid and 0.1 *N* potassium chloride. Curve I shows the effect of stopping the flow of a properly formed junction. The potential rises rapidly through a millivolt or more, and this is followed by a slow decrease of potential. It is the top of this curve that has, apparently, been considered to be the "correct" potential of the junction. At *b* on this curve the flow was started again and the original potential was quickly regained at *c*. At *d* the flow was again stopped and the potential rose to a different maximum, after which it slowly decreased. This time, at *e*, the original potential was almost instantly obtained from the higher value by starting the flowing. Curve II and III show the effect of too slow flowing, 1 and 2 drops a minute respectively dripping from the outlet tube. The

<sup>17</sup> See MacInnes, *This Journal*, 43, 1217 (1921).



dotted line represents the constant potential of the junction procured by the passage of from 3 to 7 drops a minute. Above the latter rate (from 8 drops per minute to rapid streaming) there was a perceptible decrease in the potential, but of the order of a few hundredths of a millivolt only. This was possibly due to drawing cool solutions from the reservoirs B and C into the boundary.

The phenomena underlying the curious rise of potential when the junction flow is stopped are obscure, but they are undoubtedly related to the fact that the moving junction tends to give a "mixture" boundary, *i. e.*, one in which the electrolyte concentration is constant throughout, whereas if time for diffusion is allowed there will be, immediately after stopping the flow at least, planes in the boundary at which the total concentration is greater than on either side, due to the fact that one electrolyte, in general, will have a greater diffusion constant than the other.

## 7. Experimental Results and Discussion.

The potentials at the junctions of solutions of hydrochloric acid with solutions of the alkali chlorides and of pairs of the alkali chlorides with each other, are given in Table I for 0.1 *N* solutions and in Table II for 0.01 *N* solutions. The different figures for each pair of electrolytes in the column headed "measured e. m. f." are the results of independent measurements, starting, in many cases, from freshly prepared solutions. The combination  $\text{HCl}|\text{KCl}$  at 0.1 *N* was, however, measured at least ten times with results that agreed within a few hundredths of a millivolt.

In the last column of each table the results of computations based on Lewis and Sargent's formula:  $E_1 = RT/F \cdot \ln \Delta_c/\Delta'_c$ , are given.<sup>18</sup> It is clear, on comparing this column of figures with that giving the directly measured values, that the Lewis and Sargent formula is remarkably successful in giving the order of magnitude of the liquid junction potential, but distinct variations are however to be observed. The junctions involving the potassium ion are, it will be noted, particularly far from agreement, the differences between the observed and computed values

<sup>18</sup> The following values for  $\Delta$  at 25° were used in this computation:

Substance.	0.01 <i>N</i> .	0.1 <i>N</i> .
HCl	411.6	390.4
KCl	141.4	129.0
NaCl	118.7	106.8
LiCl	108.6	96.7
NH <sub>4</sub> Cl	147.7	128.1
CsCl	144.6	...

Of these the values for the first three substances were taken from Noyes and Falk's compilation. (THIS JOURNAL, 34, 454 (1912)). The other values are computed from Kohlraush and Maltby's values at 18° and the temperature coefficients of Kohlraush and of Arrhenius, (Landolt and Börnstein, "Tabellen").

being close to 1.7 mv. at 0.1 *N* and 1.5 mv. for 0.01 *N* for each junction involving this ion. Since the mobilities of the potassium and ammonium ions are nearly equal the junction  $\text{KCl}|\text{NH}_4\text{Cl}$  would, according to any theory thus far advanced, be expected to be very low. The formula stated above gives 0.2 mv. for this junction whereas the measured potential is ten times that value. The difference between the observed and computed potentials is, however, nearly the same as that found for other combinations involving the potassium ion.

TABLE I.

POTENTIALS AT THE JUNCTIONS OF 0.1 *N* SOLUTIONS OF UNIVALENT CHLORIDES, AT 25°.

Electrolytes.	Measured e. m. f. Millivolts.	Computed e. m. f. Millivolts.	
		By difference.	Lewis and Sargent's formula.
HCl, KCl.....	26.78	26.78	28.4
HCl, NaCl.....	33.07	33.08	33.3
	33.13		
	33.07		
HCl, LiCl.....	34.87	35.65	35.8
	34.87		
	34.83		
HCl, $\text{NH}_4\text{Cl}$ .....	28.40	28.78	28.6
	28.39		
KCl, NaCl.....	6.45	6.30	4.9
	6.35		
	6.45		
KCl, LiCl.....	8.85	8.87	7.4
	8.63		
	8.89		
KCl, $\text{NH}_4\text{Cl}$ .....	2.13	2.00	0.2
	2.16		
	2.20		
NaCl, LiCl.....	2.65	2.57	2.5
	2.65		
	2.57		
NaCl, $\text{NH}_4\text{Cl}$ .....	-4.21	-4.30	-4.6
	-4.26		
	-4.15		
LiCl, $\text{NH}_4\text{Cl}$ .....	-6.93	-6.87	-7.2
	-6.92		

Since this abnormality of the potassium ion is very surprising, it was considered desirable, after the work described above was completed, to get independent measurements of some of the potentials of junctions involving that ion. With the aid of a liberal grant from the Warren Fund of the American Academy of Arts and Sciences, Mr. E. R. Smith of this laboratory repeated a number of the determinations. To be sure

TABLE II.  
POTENTIALS AT THE JUNCTIONS OF 0.01 *N* SOLUTIONS OF UNIVALENT CHLORIDES AT 25°.

Electrolytes.	Measured e.m.f. Millivolts.	Computed e. m. f. Millivolts.	
		By difference.	Lewis and Sargent's formula.
HCl, KCl.....	25.70 25.75 25.72 25.73	25.62	27.4
HCl, NaCl.....	31.12 31.19 31.18	31.19	31.9
HCl, NH <sub>4</sub> Cl.....	27.06 27.00 27.00	26.93	27.4
HCl, LiCl.....	33.77 33.79 33.70	33.82	34.2
KCl, NaCl.....	5.65 5.65	5.57	4.5
KCl, LiCl.....	8.25 8.16 8.20	8.20	6.8
KCl, NH <sub>4</sub> Cl.....	1.30 1.31	1.31	0.05
KCl, CsCl.....	0.30 0.32	0.30	0.005
NaCl, LiCl.....	2.65 2.57 2.67	2.63	2.3
NaCl, NH <sub>4</sub> Cl.....	-4.31 -4.21	-4.26	-4.5
NaCl, CsCl.....	5.40 5.41 5.36	-5.17	-5.1
LiCl, NH <sub>4</sub> Cl.....	-6.89 -6.89	-6.89	6.9
LiCl, CsCl.....	-7.78 -7.81	-7.80	-7.3
CsCl, NH <sub>4</sub> Cl.....	0.95	0.91	0.5

that the abnormality was not due to the sample of potassium chloride used, measurements were made with (a) the material used in the foregoing experiments, (b) another sample of German origin, and (c) an American product. The latter two samples were purified as described in Section 4. The potentials of 0.1 *N* potassium chloride solutions against a newly prepared 0.1 *N* hydrochloric acid solution were as follows: Sample (a) 26.70 mv., Sample (b), 26.90 mv. and Sample (c), 26.87 mv. which agree substan-

tially with the value (26.78 mv.) given in Table I. Independent determinations were also made of the potentials of the junctions:  $\text{HCl}|\text{NaCl} = 33.11$  mv., and  $\text{KCl}|\text{NaCl} = 6.38$  mv. both at 0.1 *N*, and of the junction  $\text{HCl}|\text{KCl} = 25.74$  mv. at 0.01 *N*, all of which agree closely with the potentials given in the tables above. It would appear, therefore, that the deviation of the potentials of junctions involving the potassium ion from values predicted by the Lewis and Sargent formula are real and not due to experimental error or to impurities in the materials. This later work has also demonstrated that the apparatus, though apparently complex, will give correct results with but little practice in its use. Mr. Smith is now determining the potentials at the junctions of the alkali bromides. We wish, at this point, to express our gratitude to the Committee of the Warren Fund for its assistance.

The question immediately presents itself: Why do the potassium, and to a lesser extent the lithium, ions yield potentials that cannot be computed by the Lewis and Sargent formula, when junctions involving pairs of the hydrogen, sodium, cesium, and ammonium ions can be obtained from it almost within experimental error? We have at present no answer to offer, but we hope that the matter will be cleared up by further work.

There is, however, a remarkably simple relation connecting the observed potentials in Tables I and II. At both concentrations a figure can be obtained, for each electrolyte, such that the difference between any two figures gives the corresponding liquid junction potential. A set of such figures for each concentration can be found in Table III and the results of each subtraction are given in the columns headed "by difference" in Tables I and II. The figures in Table III are, of course, averaged from the results themselves. It will be seen that, with one exception, the potentials can be found, almost within experimental error, from these figures. This relation appears to be another instance of the remarkable additivity of the properties of solutions of strong electrolytes. As is obvious from the properties of the logarithm, a similar relation would hold if all the potentials could be calculated from Lewis and Sargent's equation or from Planck's original equation. The potassium and lithium ions behave, however, as if, in this connection, they have different  $\Lambda$  values than those obtained from conductance measurements.

TABLE III.  
CHARACTERISTIC POTENTIALS.

Electrolyte.	0.1 <i>N</i> .	0.01 <i>N</i> .
$\text{LiCl}$ .....	0.0	0.0
$\text{KCl}$ .....	8.87	8.20
$\text{HCl}$ .....	35.65	33.87
$\text{NaCl}$ .....	2.57	2.63
$\text{NH}_4\text{Cl}$ .....	6.92	6.89
$\text{CsCl}$ .....	.....	7.80

### 7. Summary.

Using a slightly modified form of Lamb and Larson's "flowing" junction apparatus, reproducible values were obtained, within a few hundredths of a millivolt, of the potentials of the liquid junctions between equi-concentrated solutions of a series of monovalent chlorides. The Lewis and Sargent form of Planck's original equation,  $E_l = RT/F \ln \Delta c / \Delta' c$ , expresses the results for junctions involving most of the ions studied, and gives qualitative agreement in all cases. The experimentally determined potentials can, however, be obtained from the differences between numbers, one for each ion at each concentration. This is equivalent to the expression given above, except that, for the potassium and lithium ion, values of  $\Delta$  which are slightly different from those obtained from conductance measurements would have to be used.

CAMBRIDGE 39, MASSACHUSETTS.

### NOTES.

**A Simple Method for the Preparation of Sodium Hydroxide free from Carbon Dioxide.**—Having recently had occasion to prepare solutions of sodium hydroxide free from carbon dioxide, the method of preparation here described was evolved and in use found simpler than most methods commonly used.

**Method.**—Distilled water contained in an Erlenmeyer flask is boiled to remove any carbon dioxide present, after which, when the water is cooled enough, ethyl ether is added to form a layer 3 or 4 cm. in depth. Pieces of metallic sodium, not exceeding about 1 cm. in diameter are then dropped into the flask. They will fall no further than the ether layer where they remain suspended. The water contained in the ether layer causes the slow formation of sodium hydroxide, which readily passes below to the water layer. Meanwhile the ether prevents the results usually observed when metallic sodium is brought in contact with water in the presence of air. After the desired quantity of metallic sodium has reacted, the larger portion of ether is removed by a pipet, and the last traces by boiling the solution. Various modifications and adaptations will suggest themselves to the reader.

**Fire Hazard.**—It would seem that the above procedure is fraught with considerable danger from fire and explosions. Particular effort was made to cause explosions. As a result it was observed that none occurs so long as the depth of the ether layer is great enough so that the suspended sodium cannot simultaneously come in contact with both air and water. When the quantity of sodium to be dissolved is rather large in proportion to the quantity of ether present it sometimes happens that the heat evolved by the reaction is sufficient to evaporate the ether sufficiently to cause

fire hazard. Obviously, this condition is easily corrected by the addition of more ether to the flask. Of the explosions resulting by intentionally adding large quantities of sodium to a shallow ether layer, none was of sufficient violence to break the containing flask which, of course, was unstoppered. With the care ordinarily exercised in handling ether and by keeping the ether layer as thick as 3 or 4 times the diameter of the largest piece of sodium being dissolved, the reaction is carried out easily and without danger. A further advantage of the method arises from the fact that the greater part of any kerosene adhering to the sodium is removed with the ether.

**Purity of Product.**—No precipitate is formed when a solution of barium hydroxide is added to a solution of sodium hydroxide prepared by this method; but further than this, no critical examination has been made to learn whether or not this product is of sufficient purity for purposes requiring high precision. It is hoped to extend the work to include a study of the applicability of this method to the preparation of the hydroxides of all the alkalis and alkali earth metals and to a critical examination of the purity of the resulting products.

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Received July 30, 1921.

**The Nesslerization of Ammonia Solutions.**—In using the Folin-Bell<sup>1</sup> method for the determination of ammonia in urine and the Folin-Youngburg<sup>2</sup> method for the determination of urea in urine, we found trouble in keeping the product of the nesslerizations dissolved. This uncertainty concerning clouds and precipitates forming in nesslerized mixtures had been mentioned by Allen and Davisson<sup>3</sup> in a paper on colorimetric work. We set out to find what were the necessary conditions for a successful nesslerization that would give a solution yielding no precipitate on standing for the usual time required for the colorimetric determination.

We have found several precautions necessary. When any of these are not carefully observed the product of the nesslerization will be partly dissolved and partly precipitated. If the following precautions are taken the product of the nesslerization will be a clear sparkling solution with no visible precipitate.

1. All dilutions must be made with distilled water. Tap water, even though ammonia-free, has not been found advisable.

2. The flasks in which the nesslerizations are made should be well rinsed with c. p. nitric acid and then with distilled water to remove the mercury film that may have separated from a previous nesslerization.

<sup>1</sup> Folin and Bell, *J. Biol. Chem.*, 29, 333 (1917).

<sup>2</sup> Folin and Youngburg, *ibid.*, 38, 111 (1919).

<sup>3</sup> Allen and Davisson, *ibid.*, 40, 196 (1919).

3. The Nessler solution used should be the one recommended by Folin in his later paper.<sup>4</sup> Folin's earlier Nessler solution<sup>5</sup> was not found to work as well.

4. The given amount of Nessler solution (10 cc. to 20 cc.) must be added rapidly all at once. We found that a wide-mouthed pipet or cylinder worked very well. Slow addition of the reagent was not good.

5. After the addition of the Nessler solution, the mixture must not be shaken or stirred. It must be left perfectly quiet for at least 20 minutes. When the reagent is added, the solutions mix instantly as intimately as is possible with shaking. Any dilution with water to a definite volume must be done gently and only after the 20 minutes' standing period.

6. The solution to be nesslerized should not contain over 1.0 mg. of ammonia nitrogen for 150 cc. of solution. On nesslerization and dilution of the product to 200 cc., the brown color is very intense, and with such concentrated solutions part of the product tends to deposit on the walls of the flask and interfere with the colorimetric work.

After determining the necessary precautions we tried some 200 nesslerizations, leaving out some one or another of the above precautions. Only very rarely were we able to obtain successful results. Using the precautions mentioned, in more than 200 nesslerizations, we did not meet with a single failure. We therefore believe that the method outlined above affords complete control and gives solutions that are clear and remain so for hours. The necessary precautions are not bothersome.

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CONTRIBUTION FROM THE CHEMISTRY LABORATORIES  
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BLOOMINGTON, INDIANA.

Received August 9, 1921.

**The Preparation of Chloroplatinic Acid by Means of Hydrogen Peroxide.**—Since the use of concentrated hydrogen peroxide and hydrochloric acid instead of aqua regia for solution of platinum black in the preparation of chloroplatinic acid was first described,<sup>1</sup> the technique has been improved in several details, and it seems worth while at this time to describe briefly the method developed after several years of experience.

The presence of organic compounds, other than sodium formate, was avoided from the start and for this reason the difficulty with acetanilid

<sup>4</sup> Folin and Wu, *J. Biol. Chem.*, **38**, 89 (1919).

<sup>5</sup> Folin, *ibid.*, **26**, 473 (1916).

<sup>1</sup> Rudnick and Cooke, *THIS JOURNAL*, **39**, 633 (1917).

mentioned by Braley and Shaffer in their paper<sup>2</sup> was never encountered. The peroxide used in this work was, from the very first concentrated from a commercial product stated to be free from acetanilid, alcohol, etc.

Platinum black seems to dissolve more readily if it is not allowed to become dry after reduction. In order to combine this advantage with the necessity of keeping account of yields and of the amount of platinum in stock, the purified potassium chloroplatinate rather than the dried platinum black was chosen as the starting point for the preparation of the final solution. This offers the further advantage of starting with a pure compound for reduction and so obtaining a clean, quick and perfect separation of the platinum black.

Another important point developed was the use of hydrogen chloride instead of the strong aqueous acid. Hydrogen chloride is so easily made by the usual method of adding conc. sulfuric acid to conc. hydrochloric acid that this point offers no difficulty to offset the advantage of concentration and increased speed of solution.

The method, then, as at present used may be briefly described as follows.

The potassium chloroplatinate residues accumulating from the determinations of potash are extracted with the smallest possible quantities of boiling water and filtered while hot so as to separate all asbestos and paper fibers of the filter pads. The pure chloroplatinate crystals obtained on cooling are dried and form a part of the material for preparation of the reagent.

The filtrate and all other aqueous filtrates, including the spent Lindo-Gladding solution, are reduced with zinc and hydrochloric acid. All filtrates from this reduction are allowed to stand exposed to sunlight as much as possible for several weeks. Sometimes additional platinum black is obtained in this way.

The alcoholic filtrates are evaporated until the alcohol is driven off as judged by the odor. The residue is then reduced with zinc and hydrochloric acid and further treated in the same manner as the aqueous filtrates referred to in the preceding paragraph.

Whenever platinum black comes down in the form of a mirror, or otherwise does not lend itself readily to solution with hydrogen peroxide in a small volume, it is best to dissolve such deposits with a little nitro-hydrochloric acid. The nitric acid is evaporated and the remaining solution is added to the next lot of filtrate to be reduced with zinc and hydrochloric acid.

The more or less granular crude platinum black thus obtained is thoroughly washed by decantation and is then treated with hydrogen chloride.

<sup>2</sup> The Interaction of Platinum, Hydrochloric Acid and Hydrogen Peroxide. Presented at the April, 1921, Meeting of the American Chemical Society, Rochester, N. Y.



To this in suspension conc. hydrogen peroxide<sup>3</sup> is added and hydrogen chloride is bubbled through simultaneously in such manner that the bubbles keep the platinum black well agitated. After the flow of gas and of peroxide have been properly regulated, the process needs very little attention and solution is complete in the course of some hours, the time depending on the amount of platinum black to be dissolved.

The solution thus obtained is treated with the necessary amount of pure potassium chloride and the potassium chloroplatinate crystals are filtered off, dried and added to the stock of pure chloroplatinate on hand.

From a weighed amount of this stock the reagent is prepared by reduction with alkaline sodium formate, washing the platinum black obtained and dissolving it as described above. This solution is then made up to the proper volume as calculated from the weight of chloroplatinate taken, so that 10 cc. of the reagent contains 1 g. of metallic platinum, as required by the official methods of the A.O.A.C.<sup>4</sup>

PAUL RUDNICK.

CONTRIBUTION FROM THE CHEMICAL LABORATORIES  
OF ARMOUR AND COMPANY,  
CHICAGO, ILLINOIS.  
Received October 6, 1921.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TORONTO.]  
**FRIEDEL AND CRAFTS' REACTION. SOME SUBSTITUTED  
PHTHALIC ANHYDRIDES WITH TOLUENE AND  
ALUMINUM CHLORIDE.**

BY WALTER A. LAWRENCE.  
Received June 18, 1921.

As pointed out in a previous paper<sup>1</sup> an unsymmetrical phthalic anhydride with benzene and aluminum chloride may give two acid products. In some of the reactions described in this paper two acid products were obtained, in others only one. With the symmetrical tetrahalogenophthalic anhydrides only one acid product was obtained as was to be expected.

The physical properties of the toluyl-nitrobenzoic acids are very similar

<sup>3</sup> The conc. hydrogen peroxide should be freshly prepared immediately before use. Commercial peroxide, free from preservatives, is concentrated by distillation at reduced pressure to  $\frac{1}{10}$  its volume. The reservoir of commercial peroxide is connected to a Pyrex distilling flask, holding about twice the volume of conc. peroxide to be prepared, and the initial volume in the flask, which is the final volume desired, is maintained. The distillation is carried on under a pressure of 50 mm. of mercury or less and the bath is kept at a temperature 5° to 10° higher than the boiling point of water at the pressure in the flask.

Hydrogen chloride is prepared in the usual manner by adding conc. sulfuric acid to conc. hydrochloric acid in a suitable generator.

<sup>4</sup> Official Methods, A.O.A.C., 1920, p. 12.

<sup>1</sup> Lawrence, *THIS JOURNAL*, 42, 1871 (1920).

to those of the benzoyl-nitrobenzoic acids. They are brownish amorphous powders which do not have a sharp melting point and decompose on melting and while somewhat more soluble in hot than in cold alcohols, they do not crystallize from these solvents.

In all the acids obtained the toluene is represented as entering the reaction at the position *para* to the methyl group. The sodium, potassium and ammonium salts of all the toluyl-tetrahalogeno-benzoic acids are only slightly soluble in water. A small quantity of each of the benzoyl-tetrahalogeno-benzoic acids described by Alice Hofmann<sup>2</sup> was prepared and it was found that their alkali salts are also only slightly soluble in cold water.

**General Procedure.**—The derivative of the phthalic anhydride was treated with aluminum chloride and excess of toluene in the proportion of two mol. wts. of aluminum chloride to one mol. wt. of the anhydride. In most of the experiments about 9 g. of aluminum chloride was used and 45 to 50 cc. of toluene. After heating until hydrogen chloride ceased to come off, 10% hydrochloric acid was added, the contents of the flask were shaken and the excess of toluene distilled with steam. The residue was filtered, washed and boiled with a saturated solution of sodium carbonate. The alkaline solution was filtered and the filtrate acidified slowly with 10% hydrochloric acid.

**3-Nitrophthalic Anhydride with Toluene and Aluminum Chloride.**—The yield was 51%, calculated on the anhydride. The two isomeric acids in this precipitate have no marked solubility differences, but a somewhat unsatisfactory separation was effected by methyl alcohol.

**Identification of the Acid Less Soluble in Methyl Alcohol.**—This acid is very soluble in acetone, moderately soluble in ethyl alcohol, less soluble in methyl alcohol and almost insoluble in ether and ligroin; m. p. 262–5° (decomp.).

**Hydrolysis.**—A solution of 2 g. of the acid and 10 g. of potassium hydroxide was heated in a nickel crucible to about 215° for 20 minutes. When cold the mass was dissolved in water, filtered, acidified and the precipitate dried. When heated for several hours on the water-bath the sublimate was *p*-toluic acid and the residue was *o*-nitrobenzoic acid.

**Synthesis.**—Nine g. of 2-carbethoxy-3-nitrobenzoyl chloride<sup>3</sup> was dissolved in 45 cc. of toluene and 9.5 g. of powdered aluminum chloride slowly added. The mixture became warm and large quantities of hydrogen chloride were given off. When the initial reaction was over the mixture was heated on the water-bath for 8 to 9 hours, acidified and the excess of toluene removed. The product, a tarry viscous oil, was hydrolyzed with alcoholic potassium hydroxide, the potassium salt dissolved in water and the solution acidified. The acid was purified by dissolving in hot alcohol and allowing the solution to cool, when a light brown amorphous powder was obtained which melted

<sup>2</sup> Hofmann, *Monatsh.*, 36, 805 (1915).

<sup>3</sup> In my previous paper it was stated that the carbethoxy-nitrobenzoyl chlorides from 3-nitrophthalic acid had not previously been described. Since publication I have found that they had been described by Cohen, Woodroffe and Anderson, *J. Chem. Soc.*, 109, 234 (1916).

with decomposition at 262-5°; yield about 53%. This product, therefore, is 6-*p*-toluyl-2-nitro-benzoic acid.

*Analysis.*—Calc. for  $C_{15}H_{11}O_5N$ : N, 4.91. Found: 4.72.

*Identification of the Acid More Soluble in Methyl Alcohol.*—From a hot saturated solution of the acid in methyl alcohol a small quantity of a light brown amorphous powder was obtained which darkened at 105-7° and decomposed at 122-6°.

*Hydrolysis.*—Fusion with potassium hydroxide gave two products which were separated by sublimation. They were identified as *p*-toluic acid and *m*-nitrobenzoic acid.

*Synthesis.*—Nine g. of 6-carbethoxy-2-nitrobenzoyl chloride was dissolved in 45 cc. of toluene and 9.5 g. of aluminum chloride added slowly. The reaction began in the cold and no heat was applied for one hour. The mixture was then heated on the water-bath for 9 hours, cooled, acidified and the toluene distilled. The viscous, black, oily ester was hydrolyzed with 8% alcoholic potassium hydroxide. The acid so prepared darkened at 106-9° and decomposed at 123-6°. This product is, therefore, 2-*p*-toluyl-3-nitrobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{11}O_5N$ : N, 4.91. Found: 4.71.

**4-Nitrophthalic Anhydride with Toluene and Aluminum Chloride.**—The precipitate obtained by acidifying the sodium carbonate solution was found to consist almost altogether of an acid soluble in ethyl alcohol and melting with decomposition at 100-105° but there was a small quantity of material less soluble in ethyl alcohol melting with decomposition at 211-18°.

*Identification of the Acid Melting with Decomposition at 100-105°.*—This acid is soluble in methyl alcohol, ethyl alcohol and acetone, slightly soluble in ether and benzene and insoluble in ligroin.

*Hydrolysis.*—Fusion with potassium hydroxide for 20-25 minutes at 210-20° gave *p*-toluic acid and *p*-nitrobenzoic acid.

*Synthesis.*—Ten g. of 6-carbo-methoxy-3-nitrobenzoyl chloride was dissolved in 50 cc. of toluene and 9 g. of powdered aluminum chloride slowly added. The reaction began vigorously in the cold, and after standing for one hour the mixture was heated on the water-bath for 6-7 hours. The black viscous product obtained after acidification and removal of the toluene was hydrolyzed with 8% alcoholic potassium hydroxide redissolved in sodium carbonate solution, precipitated by acid, washed and dried; m. p. 101-5° with decomposition; yield, 55%.

This acid is, therefore, 2-*p*-toluyl-4-nitrobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{11}O_5N$ : N, 4.91. Found: 4.77.

**3-Acetyl-amino-phthalic Anhydride with Toluene and Aluminum Chloride.**—The solution obtained by using cold sodium carbonate on acidification gave an acid which on purification melted at 256-7°. The residue from the sodium carbonate solution after washing with cold benzene gave an acid which on further purification melted at 206°.

*Partial Identification of the Acid Melting at 256-7°.*—This acid is not very soluble in water but small quantities of very pure crystals may be obtained by making a saturated solution in hot water, allowing the solution to cool, and repeating this once or twice. It is soluble in ethyl and methyl alcohol. Yield about 20%, calculated on the anhydride.

*Hydrolysis.*—When fused with potassium hydroxide for 20 minutes at 200-215° and acidified only *p*-toluic acid and benzoic acid were recognized. This indicates that the aminobenzoic acid was converted into benzoic acid during the fusion.

Reduction of the *p*-toluyl-nitrobenzoic acids by ferrous sulfate and also by zinc and acetic acid was attempted, but the results were unsatisfactory, due in part to the limited amount of pure acids available.

This acid is, therefore, 2- or 6-*p*-toluyl-3- or 2-aminobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{12}O_3Na$ : Ag, 29.8. Found: 30.0.

*Partial Identification of the Acid Melting at 206°.*—This acid is not very soluble in cold sodium carbonate solution but is somewhat soluble in the hot solution. The alkaline solution was acidified and the precipitate dried; yield about 40% calculated on the anhydride used. It was recrystallized twice from ethyl alcohol. It is soluble in acetone, slightly soluble in ether and insoluble in benzene.

*Hydrolysis.*—Fusion with potassium hydroxide at 210–20° for 20 minutes gave a product from which *p*-toluic acid and a small amount of benzoic acid were obtained.

This acid is, therefore, 2- or 6-*p*-toluyl-3- or 2-aminobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{12}O_3Na$ : Ag, 29.8. Found: 29.65.

**4-Acetyl-amino-phthalic Anhydride with Toluene and Aluminum Chloride.**—The precipitate consists principally of one acid; only a small quantity of the second acid was found; yield, 62%.

*Partial Identification of the Acid Melting at 135–6°.*—The precipitate from the carbonate solution was dissolved in alcohol and water added until a faint cloudiness appeared. On standing for several hours a small quantity of gum separated; the alcohol which still contained the bulk of the material was poured off and allowed to slowly evaporate at room temperature. The second deposit was still gummy but on drying was easily powdered. Repeating this operation gave a product melting at 135–6°. It is soluble in ethyl alcohol, methyl alcohol and acetone, slightly soluble in benzene and insoluble in ether.

*Hydrolysis.*—Fusion with potassium hydroxide at 205–215° for 25 minutes gave a product from which *p*-toluic acid and a small quantity of benzoic acid were obtained.

This acid is, therefore, 2- or 6-*p*-toluyl-4- or 3-aminobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{12}O_3Na$ : Ag, 29.8. Found: 29.7.

The small quantity of material which separated first from the alcohol solution was dried *in vacuo*, dissolved in sodium carbonate solution, precipitated with acid, washed and dried; m. p. 180–3°. It is soluble in acetone and almost insoluble in benzene or ether. It is probably the isomeric acid, but sufficient quantity for identification was not obtained.

**Tetrachloro-phthalic Anhydride with Toluene and Aluminum Chloride.**—The dried product weighed 12.4 g. corresponding to a 94% yield. When recrystallized from alcohol it melted at 174.5° corr. This acid is soluble in alcohol, ether or acetone. It may be recrystallized from benzene. The sodium, potassium and ammonium salts are only slightly soluble in water.

*Hydrolysis.*—Fusion with potassium hydroxide at 210–5° for 15 minutes gave a product from which *p*-toluic acid and a small quantity of 2,3,4,5-tetrachloro-benzoic acid were obtained.

It is, therefore, 6-*p*-toluyl-2,3,4,5-tetrachloro-benzoic acid.<sup>4</sup>

*Analysis.* Calc. for  $C_{18}H_8O_3Cl_4$ : Cl, 37.5. Found: 37.1.

*Methyl Ester.*—Five g. of the acid was boiled for 50 minutes with 50 cc. of methyl alcohol and hydrogen chloride. On cooling to 10° most of the ester crystallized out. On recrystallization from methyl alcohol the ester was colorless, m. p. 96–97° (corr.). It is soluble in ethyl alcohol and acetone and slightly soluble in ether and benzene.

**Tetrabromo-phthalic Anhydride with Toluene and Aluminum Chloride.**—The dried product weighed 10.7 g. which represents an 89% yield. When recrystallized from methyl alcohol the acid melts at 212° (corr.). It may also be recrystallized from

<sup>4</sup>Brit. pat. 8917 (April 8, 1914) mentions this acid.

benzene or chloroform. It is soluble in acetone but insoluble in ether or water. The sodium, potassium and ammonium salts are only slightly soluble in water.

*Hydrolysis.*—Fusion with potassium hydroxide at 210–220° for 20 minutes gave a product from which *p*-toluic acid was isolated.

This compound is, therefore, 6-*p*-toluyl-2,3,4,5-tetrabromo-benzoic acid.

*Analysis.* Calc. for  $C_{15}H_9O_3Br_4$ : Br, 57.5. Found: 56.8.

*Methyl Ester.*—Five g. of the acid was dissolved in warm methyl alcohol containing hydrogen chloride and boiled for one hour. Most of the alcohol was then distilled off and the remainder poured into water. It was recrystallized from methyl alcohol, m. p. 162.5 (corr.). It is soluble in ethyl alcohol, benzene, ethyl acetate and ether.

*Tetra-iodo-phthalic Anhydride with Toluene and Aluminum Chloride.*—The dried product weighed 10.2 g., a 91% yield. When recrystallized from methyl alcohol or benzene it was pale yellow and melted at 266° (corr.). It is soluble in acetone and slightly soluble in water, ether and chloroform. Its sodium, potassium and ammonium salts are only slightly soluble in water.

*Hydrolysis.*—Fusion with potassium hydroxide at 200–215° for 30 minutes gave *p*-toluic acid and the acid is, therefore, 6-*p*-toluyl-2,3,4,5-tetra-iodo-benzoic acid.

*Analysis.* Calc. for  $C_{15}H_9O_3I_4$ : I, 68.25. Found: 67.9.

*Methyl Ester.*—Five g. of the acid was boiled for 1 hour with 50 cc. of methyl alcohol and hydrogen chloride and  $\frac{1}{2}$  of the alcohol was then distilled and the remainder poured into water. The ester when recrystallized from methyl alcohol was pale yellow and melted at 199° (corr.). It is soluble in alcohol, benzene and ethyl acetate and slightly soluble in ether.

### Summary.

1. The reaction of aluminum chloride and toluene with each of 7 derivatives of phthalic anhydride has been investigated.

2. Eleven new compounds have been prepared: 6-*p*-toluyl-2-nitro-benzoic acid, 262–5° (decomp.); 2-*p*-toluyl-3-nitrobenzoic acid, 123–6° (decomp.); 2-*p*-toluyl-4-nitrobenzoic acid, 101–5° (decomp.); 2- or 6-*p*-toluyl-3- or 2-aminobenzoic acid, 256–7°; 2- or 6-*p*-toluyl-3- or 2-amino-benzoic acid, 206°; 2- or 6-*p*-toluyl-4- or 3-aminobenzoic acid, 136–7°; methyl 6-*p*-toluyl-2,3,4,5-tetrachloro-benzoate, 96–7°; 6-*p*-toluyl-2,3,4,5-tetrabromo-benzoic acid, 212°; methyl 6-*p*-toluyl-2,3,4,5-tetrabromo-benzoate, 162.5°; 6-*p*-toluyl-2,3,4,5-tetra-iodo-benzoic acid, 266°; methyl 6-*p*-toluyl-2,3,4,5-tetra-iodo-benzoate, 199°.

3. The properties of 6-*p*-toluyl-2,3,4,5-tetrachloro-benzoic acid have been described.

This research was done under the direction of Professor F. B. Allan.

TORONTO, CANADA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

## HYDROXY-NAPHTHOQUINONE STUDIES. IV. NEW DERIVATIVES OF 2,3,8-TRIBROMO-5-HYDROXY-1,4-NAPHTHOQUINONE.<sup>1</sup>

BY ALVIN S. WHEELER AND T. M. ANDREWS.

Received July 22, 1921.

The papers<sup>2</sup> preceding this one dealt with (1) the reduction of naphthazarine to tetrahydroxy-naphthalene which presented a case of tautomerism of the keto-enol type; (2) the bromination of naphthazarine which revealed a case of isomerism not yet explained; (3) the chlorination and bromination of juglone or 5-hydroxy-1,4-naphthoquinone. The present investigation has extended the field which was opened up by the halogenation of juglone. It is a surprising thing that the bromination of juglone in hot glacial acetic acid solution gives a tribromo derivative in nearly quantitative yield whereas chlorination gives under similar conditions a dichloro derivative. By over-dosing the juglone with chlorine the yield is reduced and the more soluble product contains a higher percentage of chlorine but not sufficient for a trichloro-juglone. Up to the present we have been unable to prepare such a compound.

The present work more thoroughly confirms our belief that the third bromine atom is in the phenol ring, *para* to the hydroxyl group. Tribromo-juglone is a stable compound, so that there is no likelihood that two bromine atoms are attached to one carbon atom *ortho* to another carbon to which a bromine atom is joined, *i. e.*, a 2,2,3-tribromo-juglone. One bromine atom is much more reactive than the other two; hence we place it in Position 8, *para* to the hydroxyl group. All of the reactions but one in this study leave the two other bromine atoms unaffected.

The new tetrahydroxy-naphthalene (C in Fig. 1) is the simplest of the new compounds which came to light in this research. Only two of the many possible isomers have been described; (1) the 1,2,5,8-isomer described by Zincke and Schmidt<sup>3</sup> or the 1,4,5,6 as one<sup>4</sup> of us prefers to call it and (2) the 1,2,5,8-isomer of Zincke and Ossenbeck.<sup>5</sup> The new one is the 1,4,5,8-isomer. It resembles the second in its instability and was not obtained in a pure condition. It was prepared by the reduction of the dihydroxy-dibromo-naphthoquinone (B) with zinc in alkaline solu-

<sup>1</sup> This paper constitutes a portion of a thesis submitted by T. M. Andrews to the Faculty of the Graduate School of the University of North Carolina in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Wheeler and Edwards, *THIS JOURNAL*, 38, 387 (1916); Wheeler and Edwards, *ibid.*, 39, 2460 (1917); Wheeler and Scott, *ibid.*, 41, 833 (1919).

<sup>3</sup> Zincke and Schmidt, *Ann.*, 286, 37 (1895).

<sup>4</sup> Wheeler, *THIS JOURNAL*, 38, 387 (1916).

<sup>5</sup> Zincke and Ossenbeck, *Ann.*, 307, 16 (1899).



(N, O, P, Q) but *p*-nitro-aniline gave a derivative whose character we have not yet determined.

We wish to thank the National Aniline and Chemical Company of Buffalo for a supply of 1,5-dihydroxy-naphthalene which greatly aided us in this work, saving us much time in preparing this compound from naphthalene. We oxidized the dihydroxy-naphthalene to juglone in the usual way with dilute chromic acid solution. The bromination of juglone was carried out by the very smoothly working method of Wheeler and Scott.<sup>6</sup>

### Experimental Part.

**1,4,5,8-Tetrahydroxy-naphthalene (C).**  $C_{10}(OH)_4$ .—Although the bromine atoms in tribromo-juglone resist the action of acid reducing agents, they are readily affected in alkaline solution. If zinc and sodium hydroxide are employed bromine atoms 2 and 3 are replaced by hydrogen, the one at 8 by an hydroxyl group and the quinone oxygens are reduced to hydroxyl groups. One g. of tribromo-juglone is dissolved in alcohol, 40 cc. of 5% sodium hydroxide is added and the mixture heated 1 hour. This process substitutes an hydroxyl group for Bromine 8. The solution is acidified with dil. sulfuric acid, the precipitate is filtered off and washed with water. It is then added to a 30% solution of sodium hydroxide which is kept hot on a steam-bath. Zinc dust is added from time to time for 3 hours. The solution finally becomes nearly colorless except for the surface, which remains reddish. The hot solution is acidified with dil. sulfuric acid, cooled and extracted with ether. The product crystallizes from ether in plates of a light gray color. The purest product obtained melted at 224°.

*Analyses.* Subs., 0.2500:  $CO_2$ , 0.6092, 0.5926;  $H_2O$ , 0.1170, 0.1173. Calc. for  $C_{10}H_8O_4$ : C, 62.50; H, 4.16. Found: C, 64.65; H, 5.21.

**1,4,5,8-Tetrahydroxy-2,3-dibromo-naphthalene (D).**  $C_{10}H_2Br_2(OH)_4$ .—The reduction of dihydroxy-dibromo-juglone (H) was carried out by dissolving 2 g. in ether, adding dil. sulfuric acid and small portions of zinc dust from time to time, shaking well. In a few minutes the solution becomes nearly colorless. The ether layer is separated, washed with water and evaporated. The residue is pale green in color, weighs 1.8 g. and melts at 149–153°. Purification is effected by crystallizing from chloroform. The pure substance melts at 164–166° with decomposition and consists of long colorless needles which are very soluble in ether, alcohol and glacial acetic acid.

*Analyses.* Subs., 0.2210, 0.1893: AgBr, 0.2361, 0.2010. Calc. for  $C_{10}H_6O_4Br_2$ : Br, 45.71. Found: 45.48, 45.21.

**1,4,5,8-Tetra-acetoxy-2,3-dibromo-naphthalene (E).**  $C_{10}H_2Br_2(OCOCH_3)_4$ .—Two g. of the tetrahydroxy compound was boiled in 20 cc. of glacial acetic acid for 20 hours. On cooling a gummy yellowish mass separated, but it crystallized in a short time. The product weighed 2.4 g. and melted below 143°. By recrystallization of the compound several times from glacial acetic acid the melting point was raised to 149–150°. The crystals were short colorless needles. They were only slightly soluble in ether, alcohol and chloroform.

*Analyses.* Subs., 0.2174, 0.1778: AgBr, 0.1557, 0.1294. Calc. for  $C_{18}H_{14}O_8Br_2$ : Br, 30.89. Found: 30.87, 30.91.

**5-Acetoxy-8-hydroxy-2,3-dibromo-1,4-naphthoquinone (F).**  $C_{18}H_8O_5Br_2.OH.COCH_3$ .—The acetylation of the dihydroxy-dibromo-naphthoquinone of Wheeler and

<sup>6</sup> Wheeler and Scott, Ref. 2.



Scott<sup>7</sup> affected only one hydroxyl group. Three g. was boiled in 30 cc. of acetic anhydride for 17 hours. The red solution gradually became yellow, and on cooling an abundant crystallization took place. On recrystallizing from glacial acetic acid light yellow prisms were obtained. These melted at 197° to a red liquid.

*Analyses.* Subs., 0.1678, 0.1203: AgBr, 0.1600, 0.1142. Calc. for  $C_{12}H_6O_5Br_3$ : Br, 40.99. Found: 40.40, 40.58.

**1,4,5-Trihydroxy-2,3,8-tribromo-naphthalene (G).**  $C_{10}H_3(OH)_3Br_3$ .—The reduction of tribromo-juglone in acid solution is carried out as follows. To 2 g. of tribromo-juglone dissolved in 25 cc. of ether is added some 1:5 sulfuric acid and small portions of zinc dust at short intervals, the flask being well shaken. The reddish solution soon becomes pale yellow. The ether layer is separated and washed several times with water. To avoid decomposition of the product the ether is allowed to evaporate at room temperature. The crude product weighs 1.7 g., is grayish-green in color and melts at 105–106°. After recrystallizing from benzene it melts at 106–107°, and retains its light grayish-green color. It crystallizes in clusters of needles, and is soluble in ether and alcohol and slightly soluble in chloroform. It is acted upon by hot water, yielding a compound melting at 168°.

*Analyses.* Subs., 0.2022, 0.2130: AgBr, 0.2755, 0.2886. Calc. for  $C_{10}H_3O_3Br_3$ : Br, 58.11. Found: 57.98, 57.66.

A sodium salt could not be prepared by the ether-sodium carbonate method. The possibility of tautomerism caused us to try the action of ketone reagents such as hydroxylamine hydrochloride in alcoholic and in sodium hydroxide solution semicarbazine hydrochloride in potassium acetate solution (alcoholic) and nitrophenyl hydrazine. Semicarbazine alone gave a product. It was yellow and melted at 102–112° but a bromine analysis gave 39.57% instead of a calculated percentage of 51.06.

**1,4,5-Triacetoxy-2,3,8-tribromo-naphthalene (H).**  $C_{16}H_3O_6Br_3$ .—A solution of 2 g. of trihydroxy-tribromo-naphthalene in 20 cc. of acetic anhydride was boiled for 20 hours. The product crystallized on cooling as a mass of very pale yellow crystals which weighed 1.3 g. and melted at 218–220°. Recrystallization from glacial acetic acid raised the melting point to 219–220°. The crystals are very pale yellow prisms.

*Analyses.* Subs., 0.1867, 0.2303: AgBr, 0.1930, 0.2375. Calc. for  $C_{16}H_3O_6Br_3$ : Br, 44.53. Found: 43.99, 43.87.

**5-Methoxy-8-hydroxy-2,3-dibromo-1,4-naphthoquinone (J).**  $C_{10}H_2O_4Br_2OH.OCH_3$ .—Four g. of the sodium salt of tribromo-juglone was added to 800 cc. of absolute methyl alcohol containing 2 cc. of methyl iodide, and boiled under a reflux condenser for 15 hours. The purple solution after some hours gradually became red. After filtration the solution was concentrated to 25 cc. and cooled. A brick colored precipitate separated, and was filtered off and washed with a little methyl alcohol. The product weighed 3.6 g. and after recrystallizing from benzene it melted at 209–210°. The crystals are plates of a light golden-red color.

*Analysis.* Subs., 0.1533: AgBr, 0.1580. Calc. for  $C_{11}H_2O_4Br_2$ : Br, 44.20. Found: 43.86.

An attempt was made to prepare the sodium salt by shaking an ether solution with a concentrated sodium carbonate solution. The yield was small, amounting to only 15% and the content of sodium was 7.94% instead of 5.92. It appeared to change on exposure to air.

**5-Ethoxy-8-hydroxy-2,3-dibromo-1,4-naphthoquinone (K).**  $C_{10}H_2O_4Br_2OH.OCH_2CH_3$ .—Four g. of tribromo-juglone was dissolved in 1200 cc. of ether and shaken vigorously for 15 minutes with a solution of 8 g. of sodium carbonate in 80 cc. of water. The

<sup>7</sup> Ref. 6, p. 840.

precipitated sodium salt was filtered off, dried and then added to a solution of the calculated amount of ethyl iodide in 250 cc. of absolute alcohol. The solution is boiled, remains violet in color many hours and finally after 10 hours becomes reddish yellow. After concentration to 50 cc. and cooling, a light brown precipitate, weighing 3.5 g., is obtained. The crystals are thin yellow plates, some with sharply pointed ends, and melt at 134–136°. The best solvent is alcohol.

*Analyses.* Subs., 0.1959, 0.2037: AgBr, 0.1936, 0.2008. Calc. for  $C_{12}H_8O_2Br_2$ : Br, 42.55. Found: 42.06, 41.95.

The loss of one bromine atom was due to the fact that boiling alcohol removed it as demonstrated by a special experiment. Tribromo-juglone was boiled with alcohol and then gave a precipitate of silver bromide with silver nitrate.

*The Sodium Salt.*  $C_{12}H_7O_2Br_2Na$ .—One g. of the ethoxy compound, dissolved in 200 cc. of ether, was shaken for 30 minutes with 2 g. of sodium carbonate in 20 cc. of water. The reddish-purple precipitate was filtered off, washed with dil. sodium carbonate solution and ether. It dyes silk a champagne color.

*Analysis.* Subs., 0.1406:  $Na_2SO_4$ , 0.0269. Calc. for  $C_{12}H_7O_2Br_2Na$ : Na, 5.80. Found: 6.20.

5-Acetoxy-8-chloro-2,3-dibromo-1,4-naphthoquinone (M).  $C_{10}H_6O_2Br_2Cl.O.COCH_3$ .—The chloro compound described by Wheeler and Scott<sup>8</sup> was boiled with acetic anhydride for 16 hours. Dilution with water gave a mass of yellow crystals which weighed somewhat more than the chloro compound used. The product crystallized from alcohol in long light yellow prisms which melted at 159.5–160°. It is very soluble in glacial acetic acid and ether.

*Analyses.* Subs., 0.1896, 0.1563: AgBr+AgCl, 0.2554, 0.2023. Calc. for  $C_{12}H_6O_4ClBr_2$ : Cl, 8.68; Br, 39.14. If Br is assumed as correct, then Cl found is 9.27, 9.22.

8-Anilino-5-hydroxy-2,3-dibromo-1,4-naphthoquinone (N).  $C_{10}H_6O_2Br_2OH.NHC_6H_5$ .—One g. of tribromo-juglone was dissolved in 350 cc. of alcohol containing an equivalent of aniline. The solution was heated for 6 hours on a steam-bath. Crystals formed during the boiling. The yield obtained on cooling and filtering amounted to 0.8 g. The product melted at 234.5–235.5° to a red liquid and consisted of reddish-brown crystals which were rectangular with irregularly broken ends, like chips of bark. The reaction was carried out with two equivalents of aniline but the same product was obtained. The labile bromine atom at Position 8 only is affected.

*Analyses.* Subs., 0.2246, 0.2133: AgBr, 0.2010, 0.1900. Calc. for  $C_{16}H_9O_2NBr_2$ : Br, 37.82. Found: 38.10, 37.92.

8-*o*-Toluidino-5-hydroxy-2,3-dibromo-1,4-naphthoquinone (O).  $C_{10}H_6O_2Br_2OH.NHC_6H_4CH_3$ .—The *o*-toluidine derivative was prepared as described in the preceding paragraph. One g. of tribromo-juglone gave a product weighing 0.76 g. This was recrystallized from 50 cc. of acetone. The pure substance melts at 187.5–189° and consists of reddish-brown flat crystals slightly tapering to broad ends like a steel spatula.

*Analysis.* Subs., 0.1565: AgBr, 0.1353. Calc. for  $C_{17}H_{11}O_2NBr_2$ : Br, 36.61. Found: 36.80.

8-*p*-Toluidino-5-hydroxy-2,3-dibromo-1,4-naphthoquinone (P).  $C_{10}H_6O_2Br_2OH.NHC_6H_4CH_3$ .—The reaction with *p*-toluidine gave a yield of 96% of the weight of tribromo-juglone taken. The product crystallized in the hot solution. It was recrystallized from 150 parts of acetone and consisted of reddish-brown rectangular plates, melting at 216–217°. It is very soluble in ether and only slightly soluble in alcohol.

<sup>8</sup> Wheeler and Scott, Ref. 2.

*Analysis.* Subs., 0.2212: AgBr, 0.1911. Calc. for  $C_{17}H_{11}O_2NBr_2$ : Br, 36.61. Found: 36.76.

**8-*p*-Bromo-anilino-5-hydroxy-2,3-dibromo-1,4-naphthoquinone (Q).**  $C_{16}H_8O_2Br_2OH \cdot NHC_6H_4Br$ .—One g. of tribromo-juglone was boiled with 350 cc. of alcohol containing one molecule of *p*-bromo-aniline. A voluminous precipitation took place during the heating. The crude product weighed 1.2 g. and melted at 253–256°. After crystallizing twice from 75 cc. of acetone the melting point was raised only to 254–256°. The product consists of long prismatic needles of reddish-brown color, difficultly soluble in alcohol and ether.

*Analysis.* Subs., 0.1500: AgBr, 0.1691. Calc. for  $C_{16}H_8O_2NBr_2$ : Br, 47.81. Found: 47.99.

**Reaction with *p*-Nitro-aniline.**—An attempt was made to carry out the reaction with *p*-nitro-aniline. One g. of tribromo-juglone gave a yellow product weighing 0.68 g. and melting at 159.5–160° after recrystallizing twice from 50 cc. of acetone. The crystals are short yellow prismatic needles. Two determinations of bromine gave very high results, 52.31% and 52.25% instead of 34.18% calculated. We are unable to explain this at present.

**Coupling with a Diazo Compound.**—The sodium salt of tribromo-juglone was added to a diazotized solution of aniline at 0°. The product was recrystallized from alcohol, was brick-red and melted at 145–147°. No test, however, could be obtained to indicate the presence of nitrogen.

### Summary.

1. Tribromo-juglone possesses a very reactive bromine atom at Position 8. It was replaced by the following groups: OH, Cl,  $NHC_6H_5$ ,  $NHC_6H_4CH_3$  (*o*),  $NHC_6H_4CH_3$  (*p*),  $NHC_6H_4Br$  (*p*).
2. The quinone oxygens are reduced to hydroxyl groups by zinc dust in acid solution, giving a tribromo-trihydroxy-naphthalene.
3. If the bromine at Position 8 is first replaced by an hydroxyl group, then (1) zinc dust in acid solution gives tetrahydroxy-dibromo-naphthalene and (2) zinc dust in alkaline solution gives a tetrahydroxy-naphthalene.
4. The acetyl derivatives of all compounds containing an hydroxyl group were prepared.
5. The sodium salt of tribromo-juglone gave ethers on boiling with alkyl halides.
6. Compounds containing the quinoid complex and one or more hydroxyl groups are dyes.
7. All compounds described are new.

CHAPEL HILL, NORTH CAROLINA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

# THE INFLUENCE OF GLUCOSE ON THE DIALYSIS OF SUCROSE THROUGH A PARCHMENT MEMBRANE. THE POSSIBILITY OF THE SEPARATION OF GLUCOSE FROM SUCROSE BY DIALYSIS.

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Received July 25, 1921.

## Introduction.

A study of the literature has shown that the separation of glucose from sucrose by dialysis has never been attempted. Pfeffer in his classical experiments<sup>1</sup> upon osmosis in vegetable cells discovered that the osmotic pressure of dilute sugar solutions was proportional to the concentration, and that the osmotic pressure of sugar solutions underwent a regular increase with increase of temperature. And in a practical way, Dubrunfaut devised the old osmose process<sup>2</sup> for recovering sucrose from beet molasses. If beet molasses be dialyzed by means of parchment paper against running water the salts will diffuse with much greater rapidity than the sucrose and in this way the percentage of melassigenic impurities can be considerably reduced; beet molasses thus purified will deposit upon evaporation crystals of sucrose up to the new saturation point for the solution of undialyzed impurities. This process has given place technically to the saccharate process of sucrose recovery.

O. A. Val'tera<sup>3</sup> has made use of the separation by dialysis in his study of enzymes.

In order to obtain information as to whether sucrose and glucose in mixtures could be separated by dialysis and what effect glucose had on the dialysis of sucrose, five different solutions, each containing a mixture of sucrose and glucose were dialyzed through parchment paper.

## Experimental.

The materials to be dialyzed were sucrose and glucose, each containing less than 1% of impurities. Mixtures of sucrose and glucose were made up as follows: 2 g. each of sucrose and glucose in 100 cc. of distilled water; 10 g. of glucose and 25 g. of sucrose made up to 100 cc. with water; 5 g. of glucose and 25 g. of sucrose made up to 100 cc. with water; 0.5 g. of glucose and 25 g. of sucrose made up to 100 cc. with water. For the purpose of dialysis, 25 cc. of each of the above solutions was taken, and diluted to  $\frac{1}{4}$  strength for dialysis.

The dialysis was made through a parchment paper membrane. The parchment tube was made about 12.5 cm. long and 5 cm. in diameter.

<sup>1</sup> Pfeffer's "Osmotische Untersuchungen," Leipzig, 1877.

<sup>2</sup> C. A. Browne, "A Handbook of Sugar Analysis," J. Wiley and Sons Co., 1912, p. 649.

<sup>3</sup> Val'tera, "A method of Dialysis of Enzymes," *Bull. Acad. Sci. Russ.*, 1917, (6), No. 13, pp. 1075-88, abs. *Exper. Sta. Record*, 40, 111 (1921).

A solid rubber stopper was fitted into one end of the parchment tube and cemented there with paraffin. Sealing wax was first used but it was found that the wax spread on hardening and caused leaks in the joints. A 1-holed rubber stopper was fitted into the other end of the parchment tube. The sugar solution was passed into the tube by means of a 25cc. pipet. The dialysis tube was then placed in a narrow beaker and 150 cc. of distilled water was run into the beaker, thus surrounding the parchment tube. Five-cc. portions of the solution were withdrawn, two at a time, at definite intervals and placed in test-tubes. At each removal, the sucrose in one of these samples was inverted by adding 5 drops of dil. hydrochloric acid.

Bertrand's method, with slight modifications, was used in analyzing the samples. Five cc. of copper sulfate solution (from 140 g. of pure copper sulfate pentahydrate dissolved in 1000 cc. of water) and 5 cc. of a solution made up of Rochelle salt and 150 g. of solid sodium hydroxide dissolved in 1000 cc. of water were added to each of the 5 cc. samples to be analyzed. The resulting solution was placed in a small beaker and boiled for 3 minutes. The solution was filtered through asbestos in a Gooch crucible and the precipitate of cuprous oxide was washed with distilled water. The asbestos film was transferred to a beaker and 30 cc. of hot water added. The Gooch crucible was rinsed out with a hot saturated solution of ferric sulfate in 20% sulfuric acid and the rinsing run into the beaker containing the precipitate. The cuprous oxide was changed to copper sulfate by the ferric sulfate solution, a corresponding amount of which was reduced to the ferrous state. The solution was now titrated with standard potassium permanganate. The ferrous sulfate was thus oxidized to the ferric condition. By calculation the amount of cuprous oxide precipitate was determined for each sample and from this the amount of sugar corresponding to the amount of precipitated copper.

The following tables and graphs show the results of the work. The dialysis was conducted at the temperature of the laboratory, about 22.5°.

### Discussion of Results.

The results with these varying concentrations show that glucose dialyzed faster than sucrose. The influence of glucose on the dialysis of sucrose is of such a character as to keep the ratio of glucose to sucrose approximately constant after 3 hours of dialysis, irrespective of the concentration of the sucrose to be dialyzed. This can be plainly seen in Fig. 4. In Fig. 3 it is evident that the rate of the dialysis of glucose increases as the concentration of the glucose decreases, the concentration of the sucrose remaining the same.

The ratio of the percentage of the glucose to the percentage of the sucrose dialyzed is fairly constant, as seen in Tables I A, B and C, after 3 hours of dialysis; but on using a very small concentration of glucose, as in Table I D, the ratio increases approximately 2.0 times its former value.

The ratio of the dialysis of glucose to sucrose was found to be 2.5 to 1 respectively in solutions of glucose of 2% or greater; but in more dilute

TABLE IA.  
RESULTS.  
Original Solution: 2% Glucose and 2% Sucrose, 25 cc. was used for Dialysis.  
Dialysis Solution: 0.5 g. of Glucose, 0.5 g. of Sucrose, Dialyzed into 150 cc. of Water.

Time of experiment after starting dialysis.	Hours.	KMnO <sub>4</sub> solution used.	Cc.	Copper per 5 cc. of solution before inversion. (Due to glucose.)	Mg.	Copper per 5 cc. of solution after inversion. (Due to glucose and inverted sucrose.)	Mg.	Equivalent glucose per 5 cc. of solution.	Mg.	Equivalent total invert sugar per 5 cc. of solution.	Mg.	Invert sugar due to sucrose per 5 cc. of solution.	Mg.	Sucrose per 5 cc. of solution. (Calc.).	Factor (dilution).	Total glucose dialyzed.	Mg.	Total sucrose dialyzed.	Mg.	Portion of original glucose dialyzed.	%.	Portion of original sucrose dialyzed.	%.	Approximate ratio glucose to sucrose dialyzed.
0.75	(Lost)																							
0.75		0.60				5.01				2.43					30									
1.50		0.72		6.01				2.91				0.05			30		81.48		1.33		16.30		0.27 <sup>a</sup>	60.3
1.50		0.73				6.10				2.96				0.047	28									
3.5		0.94		7.85				3.81				1.13			26		99.06		27.82		19.81 <sup>a</sup>		3.96	5.0
3.5		1.22				10.19				4.94				1.07	26									
4.5	(Lost)														24									
4.5	(Lost)														24									
6.5		1.20		10.02				4.86				2.75			22		106.92				21.38			1.8
6.5		1.88				15.70				7.61				2.61	22				57.42				16.48	
0.5		0.30		2.51				1.22				0.48			30		86.60				7.32			
0.5		0.42				3.50				1.70				0.46	30				13.80					
1.0		0.55		4.59				2.28				0.20			28		62.44						2.76 <sup>a</sup>	2.7
1.0		0.60				5.01				2.43				0.19	28						12.49		1.06	11.7
3.0		1.12		9.35				4.54				0.77			26		118.04		5.32					
3.0		1.31				10.94				5.31				0.73	26				18.98		23.61		3.80	6.2
4.0		1.30		10.86				5.27							24		126.48				25.30			
4.0	(Lost)														24									
6.0		1.64		13.69				6.64				3.77			22		146.08				29.22			1.9
6.0		2.57				21.46				10.41				3.53	22				78.76				15.75	

<sup>a</sup> Probable analysis error. The column headed "Factor (dilution)" gives the number by which the mg. of glucose and sucrose from 5 cc. of the solution must be multiplied to give the total mg. of glucose and sucrose represented in the solution in the beaker.

TABLE IB.

Original Solution: 10% Glucose and 25% Sucrose; 25 cc. was used for Dialysis.

Dialysis Solution: 2.5 g. of Glucose, 6.25 g. of Sucrose, Dialyzed into 150 cc. Water.

0.5	0.42	3.50	....	1.70	....	1.36	....	30	51.0	....	2.04	....	3.3
0.5	0.75	....	6.30	....	3.06	....	1.29	30	....	38.7	....	0.62	....
1.0	0.62	5.20	....	2.52	....	2.67	....	28	70.56	....	2.82	....	2.5
1.0	1.28	....	10.70	....	5.19	....	2.54	28	....	71.12	....	1.13	....
2.0	1.05	8.77	....	4.25	....	4.74	....	26	110.50	....	4.42	....	2.4
2.0	2.22	....	18.54	....	8.99	....	4.50	26	....	117.0	....	1.87	....
3.0	1.43	11.94	....	5.79	....	6.45	....	24	138.96	....	5.56	....	2.4
3.0	2.98	....	24.88	....	12.24	....	6.13	24	....	147.12	....	2.35	....
4.5	1.82	15.20	....	7.37	....	9.14	....	22	162.14	....	6.49	....	2.1
4.5	3.98	....	33.23	....	16.51	....	8.68	22	....	190.96	....	3.06	....
5.5	3.18	26.55	....	13.02	....	16.38	....	20	260.40	....	10.42	....	2.1
5.5	6.97	....	58.20	....	29.40	....	15.56	20	....	311.20	....	4.97	....
7.0	3.37	28.14	....	13.92	....	21.69	....	18	250.56	....	10.02	....	1.7
7.0	8.33	....	69.55	....	35.61	....	20.61	18	....	370.98	....	5.93	....
24.5	8.27	69.05	....	35.40	....	25.15	....	16	566.4	....	22.65	....	3.7
24.5	13.59	....	113.47	....	60.55	....	23.89	16	....	382.24	....	6.11	....

TABLE IC.

Original Solution: 5% Glucose and 25% Sucrose; 25 cc. was used for Dialysis.  
 Dialysis Solution: 1.25 g. of Glucose, 6.25 g. of Sucrose, Dialyzed into 150 cc. Water.

Approximate ratio glucose to sucrose dialyzed.	Portion of original sucrose dialyzed.	Portion of original glucose dialyzed.	Total sucrose di- alyzed.	Total glucose di- alyzed.	Factor (dilution).	Sucrose per 5 cc. of solution. (Cal- culated.)	Invert sugar due to sucrose per 5 cc. of solution.	Equivalent total invert sugar per 5 cc. of solution.	Equivalent glucose per 5 cc. of solution.	Copper per 5 cc. of solution after in- version. (Due to glucose and invert- ed sucrose.)	Copper per 5 cc. of solution before in- version. (Due to glucose.)	KMnO <sub>4</sub> solution.	Time, drawn out after starting di- alysis.
3.5	....	3.96	70.50	49.50	30	....	2.47	....	1.65	....	3.4	0.41	0.5
....	1.13	....	....	....	30	2.35	....	4.12	....	8.5	....	1.02	0.5
4.9	....	5.87	....	73.36	28	....	2.47	....	2.62	....	5.4	0.65	1.0
....	1.21	....	75.80	....	28	2.35	....	5.09	....	10.5	....	1.80	1.0
2.1	....	8.27	....	103.32	26	....	9.86	....	3.97	....	8.18	0.98	2.0
....	....	....	243.62	....	26	9.37	....	13.83	....	27.97	....	3.35	2.0
2.5	3.90	....	....	143.76	24	....	12.74	....	5.99	....	12.35	1.48	3.0
....	....	11.50	....	....	24	12.10	....	18.73	....	37.57	....	4.50	3.0
....	4.65	....	290.40	....	24	....	....	....	9.11	....	....	2.25	4.5
2.5	....	16.03	....	200.42	22	....	18.83	....	....	55.4	18.78	6.64	4.5
....	....	....	393.58	....	22	17.89	....	27.94	....	....	....	2.55	4.5
2.2	6.30	....	....	208.60	20	....	24.59	....	10.43	....	21.29	2.55	5.5
....	....	16.69	....	....	20	23.36	....	35.02	....	68.55	....	6.64	5.5
....	7.48	....	467.20	....	20	....	....	....	....	....	....	....	5.5
1.8	....	12.89	....	161.10	18	....	27.05	....	8.95	....	18.45	2.21	7.0
....	....	....	....	....	18	25.70	....	36.00	....	70.31	....	8.42	7.0
2.5	7.40	....	462.60	....	18	....	44.73	....	21.00	....	41.9	5.02	24.5
....	....	26.88	....	336.00	16	....	....	....	....	....	....	....	24.5
....	10.88	....	679.84	....	16	42.49	....	65.73	....	122.1	....	14.62	24.5



TABLE ID.

Original Solution: 0.5% Glucose and 25% Sucrose, 25 cc. was used for Dialysis.

Dialysis Solution: 0.125 g. of Glucose and 6.25 g. of Sucrose, Dialyzed into 150 cc. of Water.<sup>1</sup>

0.5	0.20	1.67	....	0.71	....	2.53	....	30	21.30	72.00	17.04	....	14.8
0.5	0.80	....	6.68	....	3.24	....	2.40	30	....	....	....	1.15	....
1.0	0.25	2.09	....	1.02	....	4.85	....	28	28.56	129.08	22.84	....	11.0
1.0	1.45	....	12.11	....	5.87	....	4.61	28	....	....	....	2.07	....
2.0	0.27	2.25	....	1.09	....	9.24	....	26	28.34	228.28	22.67	....	6.2
2.0	2.55	....	21.29	....	10.33	....	8.78	26	....	....	....	3.65	....
3.0	0.37	3.09	....	1.50	....	13.53	....	24	36.00	308.40	28.80	....	5.8
3.0	3.66	....	30.56	....	15.03	....	12.85	24	....	....	....	4.93	....
4.5	0.41	3.40	....	1.65	....	20.04	....	22	36.30	418.88	29.04	....	4.3
4.5	5.22	....	43.59	....	21.69	....	19.04	22	....	....	....	6.70	....
5.5	0.45	3.76	....	1.82	....	23.37	....	20	36.40	444.00	29.12	....	4.1
5.5	6.01	....	50.18	....	25.19	....	22.20	20	....	....	....	7.10	....
7.0	0.55	4.59	....	2.23	....	21.44	....	18	40.14	366.66	32.11	....	5.5
7.0	5.67	....	47.37	....	23.67	....	20.37	18	....	....	....	5.87 <sup>b</sup>	....
24.5	1.15	9.60	....	4.66	....	49.12	....	16	74.56	746.56	59.65	....	5.0
24.5	12.19	....	101.78	....	53.78	....	46.66	16	....	....	....	11.94	....

<sup>b</sup> Probable slight analytical error.

solutions of glucose (0.125%), the ratio of the dialysis of glucose to sucrose was approximately 2.0 times as much or approximately 5.0 to 1, respectively.

TABLE II.  
COMPARISON OF RESULTS.

Time. Hours.	Glucose Orig. in Tube, Dialyzed.			Sucrose Orig. in Tube, Dialyzed.			Approx. Ratio of Glucose to Su- crose Dialyzed.		
	I B. %.	Tables. I C. %.	I D. %.	I B. %.	Tables. I C. %.	I D. %.	I B.	Tables. I C.	I D.
0.5	2.04	3.96	17.04	0.62	1.13	1.15	3.3	3.5	14.8
1.0	2.82	5.87	22.84	1.13	1.21	2.07	2.5	4.9	11.0
2.0	4.42	8.27	22.67	1.87	3.90	3.65	2.4	2.1	6.2
3.0	5.56	11.50	28.80	2.35	4.65	4.93	2.4	2.5	5.8
4.5	6.49	16.03	29.04	3.06	6.30	6.70	2.1	2.5	4.3
5.5	10.42	16.69	29.12	4.97	7.48	7.10	2.1	2.2	4.1
7.0	10.02	12.89	32.11	5.93	7.40	5.87	1.7	1.8	5.5
24.5	22.65	26.88	59.65	6.11	10.88	11.94	3.7	2.5	5.0
Average <sup>a</sup>							2.5	2.8	7.1

<sup>a</sup> The average is rather constant if the figures after 3 hours of dialysis are taken. In the case of the average after 3 hours of dialysis, we have for Table I B:—2.4; I C:—2.5, and I D:—4.7; and if we take the average after 3 hours of dialysis for Table I A probable experimental errors excluded, we have 2.0 for the approximate ratio of glucose to sucrose dialyzed.

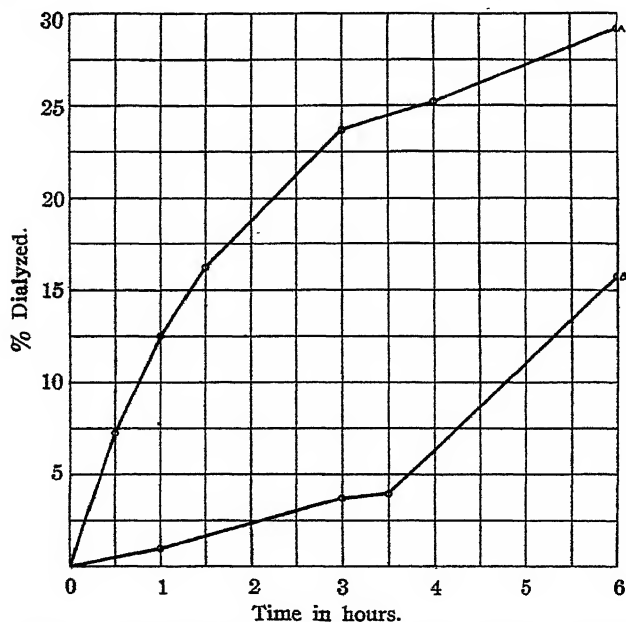


Fig. 1.—In parchment tube, 25 cc. of a solution of 2% of glucose and 2% of sucrose; dialyzed into 150 cc. of water.

A = % of the glucose dialyzed; B = % of the sucrose dialyzed.

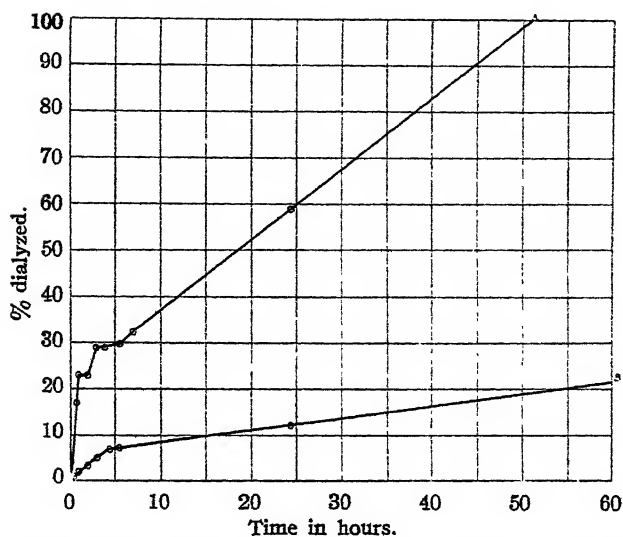
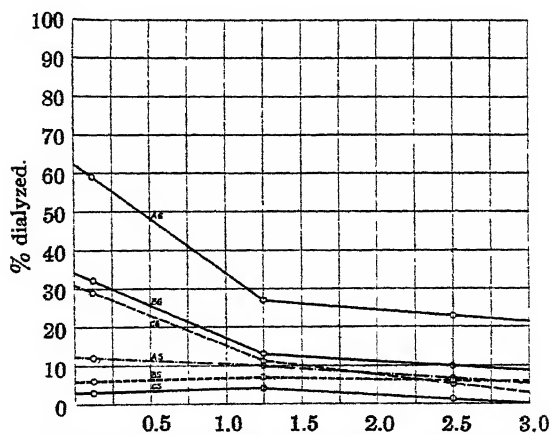


Fig. 2.—In parchment tube, 25 cc. of a solution of 0.5% of glucose and 25% of sucrose; dialyzed into 150 cc. of water.

A = % of the glucose dialyzed; B = % of the sucrose dialyzed.



Grams glucose plus 6.25 grams sucrose in tube.

Fig. 3.—AG = % of glucose dialyzed in 24.5 hours; BG, in 7.0 hours; CG, in 3.0 hours.

AS = % of sucrose dialyzed in 24.5 hours; BS, in 7.0 hours; CS, in 3.0 hours.

It is shown that in very dilute mixtures of glucose and sucrose, the former can be separated qualitatively from the latter by dialysis in about 51 hours (see Fig. 2). There is a possibility of a quantitative separation of glucose from sucrose by fractional dialysis.

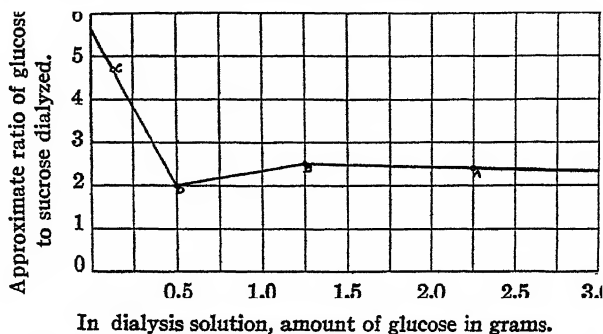


Fig. 4.—A represents 25 cc. of a solution of 10% of glucose and 25% of sucrose, dialyzed into 150 cc. of water through a parchment membrane; average after 3 hours of dialysis.  
 B=25 cc. of a solution of 5% of glucose and 25% of sucrose;  
 C=25 cc. of a solution of 0.5% of glucose and 25% of sucrose;  
 D=25 cc. of a solution of 2% of glucose and 2% of sucrose.

### Summary.

1. Five mixtures of sucrose and glucose solutions were dialyzed through parchment paper under standardized conditions and the following general facts developed as a result of the data obtained.

(a) The percentages of glucose and sucrose dialyzed in mixtures of solutions of these two substances vary inversely as the concentrations in the original solutions.

(b) In mixtures of glucose and sucrose, the influence of glucose on the dialysis of sucrose is of such a character as to keep the ratio of glucose to sucrose dialyzed approximately constant, irrespective of the concentration of the sucrose to be dialyzed, provided that the concentration of the glucose is not less than 2%, and the time of dialysis has exceeded 3 hours. In dialysis of solutions of less than 2% glucose, the glucose dialyzes much faster than at the above rate, and in 0.125% glucose solution the rate of the percentage of the glucose to that of the sucrose dialyzed is 5.0 to 1, respectively, this being 2.0 times as great a rate as in solutions of 2% or more glucose. Hence, glucose dialyzes faster than sucrose.

(c) In very dilute mixtures of glucose and sucrose, the former can be separated qualitatively from the latter by dialysis in about 51 hours. There is a possibility of a quantitative separation of glucose from sucrose by fractional dialysis.

(d) The above results apply to dilute solutions within the range covered by the experimental work.

2. The rate of dialysis was determined by removing definite volumes of the dialyzed solution at recorded intervals and inverting one portion of the removed samples to determine the percentage of sucrose calculated from the portion that was inverted.

3. Bertrand's method of analysis was used.

SYRACUSE, NEW YORK.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITIES OF TEXAS AND ILLINOIS.]

## SYMMETRICAL DI-ISOPROPYL-HYDRAZINE AND ITS DERIVATIVES.

(Preliminary Article.)

By HARRY L. LOCHTE WITH JAMES R. BAILEY AND WILLIAM A. NOYES.

Received July 26, 1921.

### Introduction.

Little work has been done on the purely aliphatic symmetrical hydrazines or hydrazo compounds and, with the exception of the stable azomethane<sup>1</sup> and certain azo derivatives of isobutyric acid,<sup>2</sup> the corresponding azo derivatives are unknown. Harries<sup>3</sup> could not isolate azoethane, and Franke<sup>4</sup> who obtained a small amount of symmetrical diisobutylhydrazine, evidently did not have enough material to study this compound at all thoroughly. Busch, in working with the latter hydrazine<sup>5</sup> does not mention the azo compound. He reports that Stolle and his coworkers made symmetrical hydrazines, but there seem to be no published articles available on this work.

The azines which are so easily prepared from hydrazine through its reaction with aldehydes and ketones, both aliphatic and aromatic, might be expected to yield, on reduction, the corresponding hydrazo compounds and thus furnish a readily available source for these substances. In some cases the reduction proceeds smoothly; *e. g.*, symmetrical benzylhydrazine ( $C_6H_5CH_2NHNHCH_2C_6H_5$ ) is easily prepared from benzalazine, ( $C_6H_5CH=N-N=CH-C_6H_5$ ). However, up to the present the reduction, in this sense, of aliphatic aldazines and ketazines has failed. Curtius, who discovered dimethyl-ketazine<sup>6</sup> ( $((CH_3)_2>C=N-N=C$

<sup>1</sup> Thiele, *Ber.*, 42, 2575 (1909).

<sup>2</sup> Thiele and Heusser, *Ann.*, 290, 30 (1896). Thiele and Stange, *Ann.*, 283, 1 (1894). Bailey and Knox, *This Journal*, 29, 890 (1907).

<sup>3</sup> Harries, *Ber.*, 27, 2279 (1894).

<sup>4</sup> Franke, *Monatsh.*, 19, 526 (1888).

<sup>5</sup> August Busch, "Über Isobutylhydrazine und Diisobutylhydrazine," *Dissertation*, Heidelberg, 1904.

<sup>6</sup> Curtius, *J. prakt. Chem.*, [2] 44, 164 (1891).

$<(\text{CH}_3)_2$ ) tried to reduce it to the symmetrical hydrazine, but he found that it is very easily decomposed into acetone and hydrazine in acid solution while alkaline reducing agents had no effect on the ketazine. Thiele attempted<sup>7</sup> to reduce this same azine, but obtained negative results with electrolytic methods he found satisfactory for the reduction of benzalazine. He also tried to prepare symmetrical di-*isopropyl*-hydrazine<sup>8</sup> through the elimination of two molecules of carbon dioxide from *isobutyric* acid, but did not succeed. Wieland<sup>9</sup> reports that the purely aliphatic aldazines are not reducible. (Presumably ketazines would be included in this statement.) It remained for Mailhe,<sup>10</sup> quite recently, to reduce ketazines. He used the Sabatier-Senderens method of catalytic reduction over hot nickel. The results obtained are of little interest however, because the main products isolated were mono- and di-*isopropylamine*.

We have become convinced, through work at the University of Texas and a continuation of this at the University of Illinois, that dimethyl-ketazine does not yield the symmetrical hydrazine with any of the ordinary neutral or alkaline reducing agents, such as aluminum amalgam, iron powder, sodium in alcoholic solution, sodium amalgam in neutral or alkaline solution, and sodium and alcohol in the presence of boric acid.

Recently, in the laboratory of the University of Texas, an exhaustive research on the use of colloidal platinum, according to the method of Skita,<sup>11</sup> in the reduction of azines and semicarbazones was begun. The present paper deals with the reduction of dimethyl-ketazine by this method and the process gives, in a yield of over 90%, symmetrical di-*isopropyl*-hydrazine that Curtius, Thiele, and Mailhe were unable to prepare by other methods of reduction. It is now possible to produce this interesting substance with little labor, in any amount desired and, no doubt, an expansion of this reaction will make available a whole series of hydrazo aliphatic hydrocarbons.

From the work of Rupe and Oestreich<sup>12</sup> it is evident that the reduction of semicarbazones presents difficulties similar to those that were encountered in the case of azines but it appears probable that the Skita method of reduction will also be found effective here.<sup>13</sup>

<sup>7</sup> Thiele, *Ann.*, 376, 262 (1910).

<sup>8</sup> Thiele and Heusser, Ref. 2.

<sup>9</sup> H. Wieland, "Die Hydrazine," Ferdinand Enke, 1913, Stuttgart.

<sup>10</sup> Mailhe, *Compt. rend.*, 170, 1265 (1920).

<sup>11</sup> Skita and W. A. Meyer, *Ber.*, 45, 3578, 3589 (1912).

<sup>12</sup> Rupe and Oestreich, *ibid.*, 45, 30 (1912).

<sup>13</sup> Neighbors and Bailey working in the laboratory of the University of Texas find that acetone semicarbazone yields very smoothly, on reduction with colloidal platinum as catalyst, carbon-amido-hydrazo-propane. A description of this phase of the work will appear shortly in *THIS JOURNAL*.

Although catalytic reduction, using platinum or palladium as catalyst and hydrogen gas as reducing agent, has been known for half a century, the possibilities of this method of reduction were not fully recognized until after the year 1900, and intensive investigation with this form of catalytic reduction really was begun in 1908. During this period three main methods were worked out: (1) the Willstätter method,<sup>14</sup> using platinum black prepared according to Low;<sup>15</sup> (2) the Paal method,<sup>16</sup> using colloidal palladium or platinum protected by the sodium salt of protalbinic or lysalbinic acid, available only for reduction in neutral or alkaline solutions; (3) the Skita method,<sup>17</sup> using gum arabic as protective colloid instead of Paal's protalbinic or lysalbinic acid. The gum arabic stabilizes the colloid in such a way that the reduction may be carried out in neutral, alkaline, or acid solution while at the end of the run the colloid is easily broken by the addition of acetone. Skita furthermore originated the principle of inoculation in catalytic reduction;<sup>18</sup> a small amount of platinic or palladous chloride is reduced separately and a few cubic centimeters of this stock solution can be employed as "seeding" colloid that aids in reducing the main mass of platinum, which, in turn, catalyzes the reduction of the substance in question.

The Skita method was selected as a promising one for the reduction of azines and has proved successful from the start. However, at first it was necessary to employ as much as 100 cc. of 10% chloroplatinic acid for every 100 cc. of ketazine. Even then with this large amount of platinum the yield was only about 80% and several days were required for completion of the reduction. In attempting to improve the yield or, at least, to reduce the amount of platinum used, it was found that partial neutralization of the base formed as the reduction proceeds immensely accelerates the reduction and makes it possible to complete this in a single day with less than a fourth of the platinum formerly used. The extra chloroplatinic acid used in our initial experiments probably owed its main effect to the hydrochloric acid liberated in this reduction rather than to the additional amount of colloidal platinum it added to the reduction mixture. Since then an article, by Skita, has appeared<sup>19</sup> in which he makes the same observation on the effect of hydrochloric acid in a similar

<sup>14</sup> Kauffman, 51, 123 (1918). Willstätter, *ibid.*, 51, 767 (1918).

Rosenmund, *ibid.*, 51, 580 (1918). Willstätter and E. W. Mayer, *ibid.*, 41, 1475 (1908).

<sup>15</sup> Low, *ibid.*, 23, 289 (1890). Willstätter and Hatt, *ibid.*, 45, 1471 (1912).

<sup>16</sup> Paal and Amberger, *ibid.*, 37, 124 (1904). Paal, *ibid.*, 45, 2221 (1912). Borsche, *ibid.*, 52, 2077 (1919).

<sup>17</sup> Skita and W. A. Meyer, *ibid.*, 45, 3579, 3589 (1912). Skita, *ibid.*, 45, 3313 (1912). Rabe, *ibid.*, 45, 2166 (1912). Skita, *ibid.*, 42, 1627 (1909); 52, 1520 (1919).

<sup>18</sup> Skita, *ibid.*, 45, 3579 (1912).

<sup>19</sup> Skita, *ibid.*, 52, 1521 (1919).

case. Further experience in these laboratories indicates that addition of hydrochloric acid is always necessary when a base is formed by catalytic reduction.

In experiments now in progress, it is found that addition of the theoretical amount of hydrochloric acid at the beginning of the run in no way diminishes the yield of 90 to 95% (based on the amount of ketazine used) that is obtained by keeping the solution only partially neutralized. Since this seems to indicate that the ketazine is not hydrolyzed appreciably by dilute acid under the conditions of our experiments, the catalytic reduction of a mixture of 1 mol of hydrazine hydrate, 1 mol. of hydrochloric acid, and 2 mols of acetone should give good results while at the same time obviating the isolation, with rather unsatisfactory yields, of dimethyl-ketazine. Three preliminary runs using, in each, 25 g. of hydrazine hydrate in 250 cc. of water gave 78, 80, and 74 g. of the hydrochloride of symmetrical di-isopropyl-hydrazine. Although only once recrystallized from alcohol, samples of this salt melted at 197–198°, had a chlorine content of 23.8% (by titration with silver nitrate), and 3 iodine titrations gave an average purity of 95.3% (2 atoms of iodine to 1 mol of the hydrazine) showing that the salt is practically pure and the yield very nearly quantitative (based on the hydrazine hydrate used), while the time required for this reduction is only 3 to 4 hours.

The hydrazo compound formed in the reduction of dimethyl-ketazine is similar to the other symmetrical hydrazines in its physical properties. It is difficult to obtain the base completely anhydrous, and it is very easily oxidized. In all reactions so far observed it is monobasic. The behavior of the base towards mild oxidizing agents is different from that of other compounds of this series.

Work on other reactions of this hydrazine and on its various oxidation products is being continued in this laboratory. It is also planned to reduce other azines of the aliphatic series, especially acetaldazine and methyl-ethyl-ketazine or methyl butyl-ketazine.

### Experimental Part.

**Reduction of Dimethyl-ketazine.**—The initial reductions were carried out on dimethyl-ketazine prepared according to the method of Curtius and Zinkeisen.<sup>20</sup> Since the yields of ketazine were only from 60 to 70% of those expected from the amount of hydrazine sulfate used, the isolation of the ketazine has been abandoned and present runs are made on a mixture of hydrazine hydrate, acetone, and hydrochloric acid. The hydrochloric acid was found necessary in case of the initial experiments and its use is essential also in runs as now made.

<sup>20</sup> Curtius and Zinkeisen, *J. prakt. Chem.*, [2] 53, 315 (1898).



The Skita apparatus<sup>21</sup> is used, the container for the reduction mixture being a liter flask. This bottle is charged with 25 g. of hydrazine hydrate (calculated from iodine titration, according to the method of Stolle,<sup>22</sup> of a solution of the hydrate) in 100 cc. of water. To this is added a mixture of 0.5 g. of gum arabic dissolved in 50 cc. of water and 10 cc. of chloroplatinic acid. The "seeding" colloid is next prepared by mixing 10 cc. of water, a few drops of gum arabic solution, 5 cc. of chloroplatinic acid, 0.5 cc. of 30% sodium hydroxide, and a few crystals of the hydrochloride of symmetrical di-isopropyl-hydrazine, or some other equally good reducing agent. On heating this mixture, reduction of the platinum begins at once. The hot mixture is rapidly added to the solution in the flask, to which are then added, under thorough shaking of the flask, 100 cc. of 18.5% hydrochloric acid and finally 100 cc. of acetone. The flask is then connected to the apparatus, the system evacuated and filled with hydrogen from a cylinder, until the apparatus is under a total pressure of 2 atmospheres. The hydrogen cylinder should be supplied with a reducing valve to prevent accidents and damage to the apparatus in filling the reservoir and flask.

The room temperature, hydrogen pressure, atmospheric pressure, and gage readings are now recorded and the shaker started. During the few minutes required for the reduction of the chloroplatinic acid the absorption is relatively slow, but as reduction of the platinum proceeds the rate of absorption increases until the gas is used up at the rate of 8 to 12 liters an hour. As reduction proceeds the absorption of hydrogen gradually slows down and comes to a complete stop at the end of 3 to 4 hours, when the theoretical amount of hydrogen has been absorbed. Enough heat is generated to keep the reduction mixture at a temperature of about 45° during the first 2 hours of the run. In case of poisoning of catalyst or other cause of slow reduction an additional 5 cc. of chloroplatinic acid is sometimes required to complete the reduction. As stated in the introductory part of this paper, the yields on 3 consecutive runs using, in each, the amount of hydrazine hydrate given above, gave yields of 78, 80, and 74 g. of hydrochloride of symmetrical di-isopropyl-hydrazine.

This salt is of about 93% purity so that the yield is practically quantitative, as the calculated yield is 76.2 g. of the hydrochloride.

**Symmetrical Diisopropyl-hydrazine.**—The reaction mixture, from the machine, is treated with acetone until the platinum and gum arabic precipitate together in the form of flakes, then filtered through a pleated filter, the filtrate acidified with hydrochloric acid and the solution evaporated to dryness *in vacuo* on a water-bath. The crude hydrochloride is slightly yellow and hygroscopic, but after recrystallization from alcohol the salt is pure white and nonhygroscopic. The free base is obtained from the salt by treatment with concentrated sodium hydroxide, the yellow oily layer separated, dried for 12 to 15 hours over solid potassium hydroxide, the base again separated and dried for 1 day with aluminum amalgam. The oil is then rapidly filtered from the inorganic material and fractionated. The base is now of a light straw color and distills between 110° and 124.5° as a colorless mobile liquid of ammoniacal, ethereal odor. A complete analysis of the 124° to 124.5° fraction as well as hydrochloric acid and iodine titrations shows this to be the pure symmetrical diisopropyl hydrazine. Even air very readily oxidizes this hy-

<sup>21</sup> Skita and Meyer, *Ber.*, 45, 3589 (1912).

<sup>22</sup> Stolle, *J. prakt. Chem.*, [2] 66, 332 (1902)

drazo compound and this property makes aluminum amalgam far superior to barium oxide, which is usually employed as a dehydrating agent for hydrazines.<sup>23</sup> In attempts to dry with barium oxide as much as 50% of the base is often oxidized to the product boiling at 88.8°, and even when an inert gas is kept over the mixture a considerable loss occurs.

The estimation of carbon and hydrogen in symmetrical diisopropyl-hydrazine presents certain difficulties which may be overcome by running the combustion very slowly on a gas furnace under the following conditions. In the beginning with only the burners next to the absorption apparatus lighted, a very slow stream of air (oxygen causes small explosions) is passed through the tube and from time to time, after the liquid in the bulb begins to vaporize, an ice pack is applied to the bedplate immediately under the sample to keep down the tendency of the combustion to run wild. On the other hand when the vaporization does not proceed fast enough a hot tile is held over the sample for a few seconds. Through this alternate cooling and heating the rate of vaporization and combustion is very carefully regulated until all of the liquid has been expelled from the bulb. The tendency of the combustion to run wild is due to the ease with which the hydrazo compound and, to a lesser extent, its derivatives are oxidized, rather than to volatility. Franke<sup>4</sup> experienced a similar difficulty in the analysis of symmetrical diisobutyl-hydrazine with a boiling point of 170–175°. After the sample has been volatilized as described above, the combustion is completed in the usual manner.

*Analyses.* Calc. for  $C_6H_{12}N_2$ : C, 62.08; H, 13.80; N, 24.14. Found: C, 62.39, 62.17; H, 13.97, 14.31; N, 24° 54, 24.30.

This sample boiled at 124° to 124.5° under 740 mm.;  $n_D^{23^\circ}$ , 1.4087;  $d_4^{31^\circ}$ , 0.7712.

Since the substance is very easily oxidized, a convenient and rapid check on its purity is obtained by titration with iodine according to Stolle.<sup>22</sup>

**Hydrochloride of Symmetrical Diisopropyl-hydrazine.**—The crude product mentioned above, recrystallized 3 times from alcohol, is obtained in the form of colorless needles melting at 198° (corr.). It is readily soluble in water and alcohol and practically insoluble in ether, acetone and benzene. The salt, like the base, is readily attacked by all common oxidizing agents. A peculiar reaction in this connection is the quantitative oxidation of the dry hydrochloride by dry copper oxide to a product boiling at 88.8° under 740 mm. pressure. A mixture of the substances, after a few minutes, gives the characteristic odor of the oxidation product. After 24 hours it becomes pasty, and finally the greenish-straw colored product is present in such amount that the whole mass may be poured out of the flask. There are reasons for believing that this is the azo compound corresponding to the symmetrical diisopropyl-hydrazine, but work on this product is still in progress and will be reported in a later article.

The hydrochloride of diisopropyl-hydrazine is so easily oxidized that nitrogen determinations may be made by simply oxidizing the salt by means of a dichromate-sulfuric acid mixture and collecting the nitrogen as usual in wet methods. Kjeldahl determinations made in the ordinary manner as well as qualitative nitrogen tests fail because of the ease with which nitrogen is split out.

*Analyses.* Calc. for  $C_6H_{12}N_2Cl$ : Cl, 23.27; N, 18.36. Found: Cl (Carius) 22.99, (titration  $AgNO_3$ ) 23.77, 23.75, 23.78, 23.69; N, (Dumas) 18.21, (sulfuric-dichromate wet method) 18.15.

**Diisopropyl-phenylthio-semicarbazide**,  $(CH_3)_2CHNH(CSNC_6H_5)CH(CH_3)_2$ .—An aqueous solution of the base treated, under cooling, with phenyl mustard oil gives

<sup>23</sup> Harries and Klamt, *ibid.*, 28, 504 (1895). Harries, *ibid.*, 31, 56 (1898).

Knorr and Kohler, *ibid.*, 39, 3259 (1906).

a good yield of a white flaky condensation product. Recrystallized from ether it melts at  $129.5^{\circ}$  (corr.). It is soluble in acetone, chloroform, benzene and ether and but slightly soluble in water, alcohol and ethyl acetate.

*Analyses.* Calc. for  $C_{12}H_{21}N_3S$ : S, 12.75; N, 16.74. Found: S(Carius) 12.45, 12.45; N, (Dumas) 16.73.

In addition to the compounds studied and analyzed the potassium cyanate and the phenyl-isocyanate condensation products and the oxalic acid salt are obtained as well crystallizing compounds, while the benzoyl compound shows no tendency to crystallize.

### Summary.<sup>24</sup>

1. Dimethyl-ketazine is reduced to the symmetrical diisopropylhydrazine by means of the Skita method of catalytic reduction.
2. The properties of the hydrazine and of some of its salts and derivatives are described.
3. Other derivatives and their reactions are being studied and are to be reported on in a later article.

AUSTIN, TEXAS; AND URBANA, ILLINOIS.

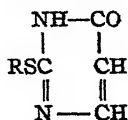
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

## RESEARCHES ON PYRIMIDINES. XCI. ALKYLATION OF 2-MERCAPTO-PYRIMIDINES.

By WILLIAM J. HORN.<sup>1</sup>

Received July 28, 1921.

When a 2-mercapto-6-oxypyrimidine combination is subjected to alkylation in alkaline solution, it is susceptible to attack in three different positions and, at the present time, we have no law, or rule, which will permit one to predict the configuration most likely to be formed.



In most of the cases so far examined<sup>2</sup> where the radical, R, of the 2-mer-

<sup>24</sup> The preparation of symmetrical diisopropyl hydrazine was effected by Bailey and Lochte at the University of Texas and the work was transferred later by Mr. Lochte to the University of Illinois. Professor Bailey prefers the name 2-hydrazopropane.

<sup>1</sup> This paper was constructed from a dissertation presented by William John Horn to the Faculty of the Graduate School of Yale University, in June, 1921, in candidacy for the degree of Doctor of Philosophy. (T. B. Johnson).

<sup>2</sup> Johnson and Clapp, *J. Biol. Chem.*, **5**, 51 (1908); Johnson and Heyl, *Am. Chem. J.*, **37**, 628 (1907); Wheeler and Johnson, *ibid.*, **42**, 30 (1909); Johnson and Jones, *ibid.*, **40**, 538 (1908); Johnson and Derby, *ibid.*, **40**, 444 (1908); Wheeler and McFarland, *ibid.*, **42**, 101 (1909); Wheeler and Liddle, *THIS JOURNAL*, **30**, 1152 (1908); Johnson and Zee, *Am. Chem. J.*, **49**, 287 (1913).

capto group has been strongly positive in nature, the alkylation reactions have been productive quite generally of isomeric 1- and 3-nitrogen substituted pyrimidines, and there seems to be no regularity in the proportion in which such isomers are produced. Regarding the mechanism of these reactions we have no very positive evidence, but it has been assumed as very probable, that all these changes take place primarily by addition of the alkyl halide to the sodium salt of the pyrimidine, which is followed by dissociation of the resulting polymolecular combination giving the alkylated pyrimidine as the final product of reaction. The configuration obtained will depend entirely upon the constitution of the primary addition product.

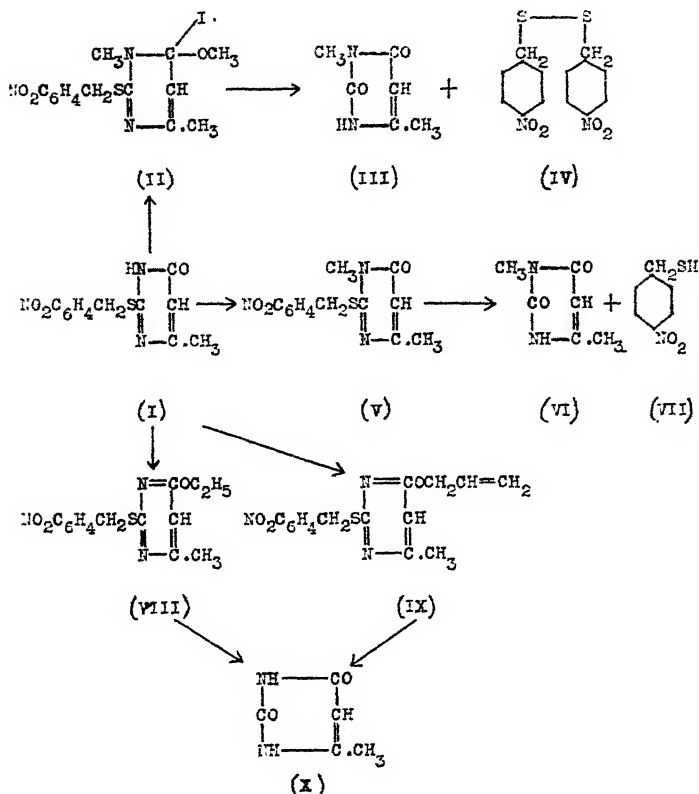
In some cases, however, it has been observed,<sup>3,4</sup> especially when the radical R of the 2-mercapto group is negative in character, that the product of alkylation is not a nitrogen pyrimidine derivative, but one in which the substitution of the alkyl group has taken place on oxygen in the 6-position of the pyrimidine cycle with formation of an alkoxyl or imido ester combination. Such transformations may be interpreted as taking place through direct substitution, although it is not improbable that the addition theory of reaction may apply also in these cases. In fact, the results obtained by Johnson and Moran<sup>4</sup> on pyrimidine alkylations, where alcoholysis of imido ester combinations was observed to take place, would seem to be very strong evidence in support of the fact that we have to deal with intermediate addition products in this type of change also.

We now describe in this paper another series of alkylation experiments which have revealed further abnormalities in chemical behavior during the process of alkylation. We have substituted the negative radical, *p*-nitrobenzyl,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$  for R and synthesized the mercapto-pyrimidine represented by Formula I. This compound is easily prepared by the action of *p*-nitrobenzyl chloride on the sodium salt of 2-thio-4-methyluracil.

Alkylation of this 2-mercapto-pyrimidine (I) with methyl iodide leads to the formation of two products which are not isomeric. The data thus far obtained indicate that the methyl group substitutes in methyl alcohol solution to give only one product, namely, 1,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine, (V). The structure of this compound was established by its behavior on hydrolysis when it was found to be transformed smoothly into *p*-nitrobenzyl mercaptan (VII) and 1,4-dimethyluracil (VI). We obtained no evidence of the formation of an isomeric, 3,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine or an imido ester combination resulting from substitution on oxygen in the 6-position of the ring.

<sup>3</sup> Johnson and Haggard, *THIS JOURNAL*, 37, 177 (1915).

<sup>4</sup> Johnson and Moran, *ibid.*, 37, 2591 (1915).



The second product of reaction with methyl iodide proved to be an addition compound, which we have expressed by Formula II. Not only is this interesting substance formed by direct alkylation of (I) with an excess of methyl iodide, but the same combination results also by interaction of the pyrimidine V with methyl iodide when digested in methyl alcohol. Hydrolysis of this substance with hydrochloric acid led to the formation of 1,4-dimethyluracil (VI), proving that the second methyl group does not link itself to nitrogen. The choice between the two other possible linkings, namely, addition to sulfur of the mercapto group or oxygen in the 6-position of the ring was indicated by the behavior on hydrolysis. By this treatment the mercapto group of the addition compound was replaced and identified as *p*-nitrobenzyl disulfide (IV). This sulfide is formed by oxidation of nitrobenzyl mercaptan, a change that is brought about by the influence of traces of iodine also formed as a product of hydrolytic change. In other words, we obtained no evidence of the formation by hydrolysis of the sulfide  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SCH}_3$ .<sup>5</sup>

<sup>5</sup> The study of these addition compounds will receive attention in the immediate future. (T. B. J.)

This is the first case to be described where we have been able to isolate an addition product of this type, and the result indicates that such combinations have probably resulted in previous condensations and that their formation is a partial explanation of the low yields and abnormal results obtained in many cases. Johnson and Jones<sup>6</sup> have shown that the pyrimidine, 2-ethyl-mercapto-3-methyl-5-ethoxy-6-oxypyrimidine, combines with potassium iodide to form a characteristic addition product. Our addition product, II, was absolutely free from inorganic material.

The fact that iodine is formed by hydrolysis of the addition product (II) in acid solution is strong evidence that the alkyl halide has dissociated in the process of addition to the pyrimidine and this condition is expressed by the structural formula assigned. The identification of this addition product is strong evidence in support of the assumption that all these alkylations in the pyrimidine series probably operate through the intermediate formation of addition compounds.

Ethyl bromide and allyl bromide interact with the sodium salt of the mercapto-pyrimidine in an entirely different manner from methyl iodide. In neither case did we observe the formation of nitrogen-substituted derivatives, but both halides interacted to form imido ester combinations. The structures of these compounds are expressed by Formulas VIII and IX respectively. The constitution of both of these pyrimidines was established by the fact that they underwent hydrolysis with formation of 4-methyluracil and nitrobenzyl-mercaptan.

In the experimental part of this paper are recorded some new facts bearing on the chemistry of *p*-nitrobenzyl-mercaptan and its corresponding sulfide derivatives.

### Experimental Part.

**2-Thio-4-methyluracil and *p*-Nitrobenzyl Chloride.**—The method employed for the preparation of 2-thio-4-methyluracil was that used by Wheeler and McFarland;<sup>7</sup> *p*-nitro-benzyl chloride was prepared according to the directions of Alway.<sup>8</sup>

**2-*p*-Nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine. (I).**—This pyrimidine was obtained in quantity by the action of *p*-nitrobenzyl chloride upon the sodium salt of 2-thio-4-methyl-uracil.

To sodium ethylate solution, prepared by dissolving a molecular proportion of sodium in absolute alcohol, finely pulverized 2-thio-4-methyl-uracil was added. On heating this mixture for two hours and shaking occasionally, the sodium salt separated and the solution became reddish-yellow in color. *p*-Nitrobenzyl chloride was then added and the resulting solution was heated until it became neutral. The solution, turned green at first and then dark red. After it had been heated for about 20 minutes it solidified to a white cake. At the end of the reaction, the mixture was cooled, filtered with the aid of suction and the crystalline product was treated with cold water to dissolve the sodium chloride formed in the reaction. The yield of crude pyrimidine was

<sup>6</sup> Johnson and Jones, *THIS JOURNAL*, 31, 590 (1909).

<sup>7</sup> Wheeler and McFarland, *Ref. 2*.

<sup>8</sup> Alway, *THIS JOURNAL*, 24, 1060 (1902).

93%. This compound is only slightly soluble in hot alcohol and difficultly soluble in hot water. It was purified by recrystallization from glacial acetic acid, from which it separated in the form of rosetts of colorless needles. These were collected on a filter, washed, first with a little acetic acid and then with water, and dried at 115° for 10 to 15 hours. By this procedure, an 80% yield of the pure compound was obtained; it melted at 220° to give a clear yellow oil.

*Analyses.* Calc. for  $C_{12}H_{11}O_3N_3S$ : N, 15.16; S, 11.55. Found: N, 15.24, 15.6; S, 11.42.

#### Alkylation of 2-*p*-Nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine.

##### Action of Methyl Iodide.

To a sodium methylate solution, made by dissolving a molecular proportion of sodium in methyl alcohol, finely pulverized 2-*p*-nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine was added and the clear greenish-yellow solution thus obtained was heated for one hour. By means of a dropping funnel, slightly more than the calculated quantity of methyl iodide was then added slowly to the warm solution of the sodium salt and the solution was heated until it became neutral. Upon removal of the alcohol by evaporation under diminished pressure, a greenish-yellow solid separated which had the odor of parsnips. This product was triturated with cold water to dissolve sodium iodide, and the insoluble material collected on a filter was dried in a vacuum desiccator over sulfuric acid for several days. This substance gave a very strong test for iodine on treatment with sulfuric acid. When the finely pulverized product was extracted in a Soxhlet apparatus with dry ether free from alcohol for 25 hours, it was separated into two distinct compounds, one of which (A) was soluble in ether and the other (B) insoluble.

(A) 1,4-Dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine. (V).—On evaporating the ether solution containing the soluble compound (A) to dryness in the air, a yellow solid was obtained which represented 71.5% of the weight of the total alkylated products. This compound was free from iodine and melted between 90° and 111°. Upon recrystallization from glacial acetic acid, it was obtained in the form of rosetts of white needles which melted sharply at 136° to give a clear yellow oil. It was identified as a monomethyl derivative of the original pyrimidine.

*Analyses.* Calc. for  $C_{12}H_{13}O_3N_3S$ : N, 14.4. Found: 14.14, 14.16.

**HYDROLYSIS WITH HYDROCHLORIC ACID.**—The structure of this compound was established by its behavior on hydrolysis with conc. hydrochloric acid. One to three g. of the compound was digested in 100 cc. of the acid for several hours. In about 10 minutes, the boiling solution became turbid and a yellowish-brown oil separated on the surface of the liquid. At the end of the reaction period, the solution was filtered to remove the oil and the filtrate evaporated to dryness. By this procedure, a yellowish-white residue was obtained which melted at 256–258°; the yield was nearly quantitative for 1,4-dimethyluracil. After recrystallization from hot water and treatment with Norite, the substance was obtained in the form of colorless prismatic needles free from sulfur. These crystals melted sharply at 259–260° to give a clear red oil.

*Analyses.* Calc. for  $C_8H_8O_2N_2$ : N, 20.0. Found: 19.93, 19.72.

The yellowish-brown oil insoluble in water solidified as it cooled to give a pearl-white solid. Dried in a vacuum desiccator over sulfuric acid the substance was obtained in quantity corresponding very closely to the quantitative yield for *p*-nitrobenzyl-mercaptan. This compound is only very slightly soluble in water, but is very soluble in ether. It was purified by recrystallization from alcohol from which it separated in the form of white transparent plates melting sharply at 58° to a clear yellow oil. A molecular-weight determination was made by the freezing-point method.

*Analyses.* Calc. for  $C_7H_7O_2NS$ : N, 8.28; S, 18.93; Mol. wt., 169.0. Found: N, 8.13, 8.47; S, 18.54; Mol. wt., 160.2, 164.8.

A further description of this compound is given below in the section devoted to the chemistry of nitrobenzyl-mercaptan.

(B) The Addition Product of Methyl Iodide and 1,4-Dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine. (II).—The insoluble amorphous compound (B) which was yellowish-brown in color, was observed to turn red slowly on exposure to the air, a behavior which was due evidently to the liberation of iodine. After drying this compound in a vacuum desiccator over sulfuric acid for several days, the weight was found to correspond to 28% of the weight of the total alkylated products. In a repetition of the alkylation with methyl iodide with a quantity of the iodide greater than that previously used, as high as 50% of the insoluble addition compound was obtained in this reaction. This product did not melt sharply; the melting point ranged between 79° and 136°. It gave a very strong test for iodine when treated with sulfuric acid and left no residue when heated on platinum foil. When boiled in 50% alcohol, it was found to dissociate, and the cool solution deposited white needle-like crystals. The compound formed melted at 136° and was identified as 1,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine.

The addition compound was purified by dissolving it to saturation in hot 80% alcohol, filtering off any undissolved material and cooling the solution immediately in an ice-bath, with stirring. By this procedure the compound was obtained in the form of a light brown colloidal precipitate. It was collected and washed with a little 80% alcohol, and dried in a vacuum desiccator over sulfuric acid for several days. Yield, 61%. It melted between 65–75° with slight decomposition.

*Analyses.* Calc. for  $C_{14}H_{16}O_4N_2SI$ : N, 9.69. Found: 9.50, 9.39.

**HYDROLYSIS WITH HYDROCHLORIC ACID.**—From 1 to 5 g. of the addition compound was hydrolyzed by digestion with 50 cc. of conc. hydrochloric acid for several hours. During this operation a yellowish-brown oil separated which solidified immediately when cooled. The yellow solution was then filtered and the residue dried and saved. This compound was identified as *p*-nitrobenzyl disulfide. The yield was nearly quantitative. Two recrystallizations from alcohol gave a product which separated in the form of colorless needles melting at 126° to give a clear yellow oil. A molecular-weight determination was made by the boiling-point method.

*Analyses.* Calc. for  $C_{14}H_{12}O_4N_2S_2$ : N, 8.33; S, 19.05; Mol. wt., 336.0. Found: N, 8.02, 8.34; S, 19.02, 19.09; Mol. wt., 334.5, 346.2.

A further description of this compound and its properties is given in the section dealing with the chemistry of *p*-nitrobenzyl-mercaptan.

The yellow acid filtrate was extracted several times with ether. On evaporating the solvent a crystalline solid was obtained which was identified as free iodine.

When the filtrate from the ether extractions was evaporated to dryness, a grayish-black solid was obtained. The residue was treated with a little cold alcohol to remove traces of iodine, and then recrystallized twice from hot water and decolorized by treatment with Norite. As the solution cooled, the compound separated in the form of white prismatic needles. The melting point, 259–260°, indicated that we were dealing with dimethyluracil.

When the pyrimidine, 1,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine (A) was hydrolyzed with conc. hydrochloric acid to which a little free iodine had been added, the results were similar to those obtained by hydrolysis of the above addition compound. That is, *p*-nitrobenzyl disulfide and 1,4-dimethyluracil were formed in this reaction.

**Synthesis of the Addition Product from its Components.**—To synthesize the addition



compound, methyl iodide (3 moles) was added to a warm alcohol solution of 1,4-dimethyl-2-*p*-nitrobenzyl-mercapto-6-oxypyrimidine and the solution was boiled for 12 hours. As it cooled, yellow needle-like crystals separated. These were found to be free from iodine and after recrystallization from glacial acetic acid, melted at 136°, which corresponds to the melting point of the unaltered mercapto-pyrimidine. After the removal of the methyl alcohol and methyl iodide from the filtrate by distillation, a light brown product was obtained. This gave a very good test for iodine. Digestion with hydrochloric acid transformed it smoothly into *p*-nitrobenzyl disulfide, which melted at 135.5°, and 1,4-dimethyluracil, melting at 260°.

#### Alkylation with Ethyl Bromide.

**2-*p*-Nitrobenzyl-mercapto-4-methyl-6-ethoxy-pyrimidine.** (VIII).—2-*p*-Nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine was added to a sodium ethylate solution made by dissolving a molecular proportion of sodium in absolute alcohol, and the solution was heated for 3 hours. A little more than the molecular quantity of ethyl bromide was then added slowly through a dropping funnel and the solution was heated until it became neutral. The hot solution was filtered to remove sodium bromide, and as the filtrate cooled, rosetts of needle-like crystals separated. After filtering and treating the residue with a little water to remove any traces of sodium bromide, the above pyrimidine was obtained; it melted between 90° and 96°. Recrystallization from alcohol gave a product which melted sharply at 104°. Yield, about 32%.

*Analyses.* Calc. for  $C_{14}H_{15}O_3N_3S$ : N, 13.77. Found: 13.70, 13.90.

**HYDROLYSIS WITH HYDROCHLORIC ACID.**—From 1 to 3 g. of this compound was hydrolyzed by digestion with 100 cc. of conc. hydrochloric acid for 3 hours. The solution was filtered to remove the oil which separated and evaporated to dryness, yielding a yellowish-white solid. This compound was identified as 4-methyluracil. It was obtained in the form of white prismatic needles which crystallized from water and did not melt below 300°. The yield was quantitative.

*Analyses.* Calc. for  $C_5H_6O_2N_2$ : N, 22.22. Found: 22.24, 22.38.

When the oily product formed in this reaction was cooled, it solidified to form a pearl-white solid which corresponded in quantity very closely to the calculated yield for *p*-nitrobenzyl-mercaptan. After recrystallization from alcohol, it was obtained in the form of white transparent plates melting at 57° to give a clear yellow oil. A mixture of this compound with *p*-nitrobenzyl-mercaptan obtained in a previous experiment melted at 57–58°.

#### Alkylation with Allyl Bromide.

**2-*p*-Nitrobenzyl-mercapto-4-methyl-6-allyloxy-pyrimidine.** (IX).—To sodium ethylate solution made by dissolving a molecular proportion of sodium in absolute alcohol, 2-*p*-nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine was added and the solution was heated for 2½ hours. Allyl bromide (1 mol.) was then added slowly through a dropping funnel and the resulting solution was heated until it became neutral. On removal of the alcohol by distillation, a soft, sticky, dark red solid separated. This was dried in a vacuum desiccator over sulfuric acid for several days, and then extracted in a Soxhlet apparatus with dry ether free from alcohol. By this procedure two compounds were obtained; a compound insoluble in ether, which proved on purification to be unaltered material, and a compound soluble in ether.

When ether solution of the soluble compound was evaporated to dryness in the air, a reddish-yellow residue was obtained. After two recrystallizations from ligroin the compound was isolated in the form of light yellow needles which melted at 77–78° to form a clear yellow oil.

*Analyses.* Calc. for  $C_{13}H_{13}O_2N_3S$ : N, 13.25. Found: 13.42, 13.52.

**HYDROLYSIS WITH HYDROCHLORIC ACID.**—A small quantity of this compound was hydrolyzed by digestion with 100 cc. of conc. hydrochloric acid for  $1\frac{1}{2}$  hours. The hot solution was filtered to remove the oil which separated and the filtrate was evaporated to dryness. A nearly quantitative yield of 4-methyluracil was thus obtained which, on recrystallization from water, did not melt below  $300^\circ$ .

By recrystallization of the oily product from alcohol, white transparent plates were obtained which melted at  $57^\circ$  to give a clear yellow oil.

### The Chemistry of *p*-Nitrobenzyl-mercaptan.

When we endeavored to identify *p*-nitrobenzyl mercaptan ( $NO_2C_6H_4CH_2SH$ ), formed in the hydrolysis of some of the 2-mercapto-pyrimidines, unexpected results were obtained. We obtained a product which melted consistently at  $58^\circ$ , while the melting point assigned to this compound in the literature is  $140^\circ$ . This marked discrepancy led us, therefore, to an investigation of the properties of this mercapto compound and its corresponding sulfide derivatives. We found that our product melting at  $58^\circ$  gave analytical results in complete agreement with those required for the mercaptan. When this compound was subjected to oxidation in the presence of iodine, or with potassium permanganate, or air in the presence of ammonia, it was transformed into the disulfide  $(NO_2C_6H_4CH_2)_2S_2$  melting at  $126.5^\circ$ . Price and Twiss<sup>9</sup> give the melting point of this compound as  $126.5^\circ$ . It was prepared by these chemists by the action of sodium carbonate upon *p*-nitrobenzyl thiosulfate.

Strakosch,<sup>10</sup> who investigated the preparation of *p*-nitrobenzyl-mercaptan, prepared it by the action of potassium hydrosulfide and ammonium sulfide upon *p*-nitrobenzyl chloride and states that these reactions lead to the formation of *p*-nitrobenzyl-mercaptan melting at  $140^\circ$ . He also states that, in the case of the action of ammonium sulfide upon *p*-nitrobenzyl chloride, prolonged boiling leads to the formation of *p*-nitrobenzyl disulfide which he describes as melting at  $89^\circ$ . On repeating his work, with potassium hydrosulfide as a reagent, it was impossible to isolate any of the compounds which he describes. Furthermore, it was found that ammonium sulfide reacts with *p*-nitrobenzyl chloride in alcoholic solution to give only the sulfide  $(NO_2C_6H_4CH_2)_2S$  melting at  $158$ – $159^\circ$ .

When *p*-nitrobenzyl chloride was treated with sodium hydrosulfide in alcoholic solution, we obtained two compounds; the disulfide melting at  $126^\circ$ , and the sulfide melting at  $158$ – $159^\circ$ . This compound corresponds to *p*-nitrobenzyl sulfide described by O. Fischer.<sup>11</sup>

The interesting results obtained with *p*-nitrobenzyl-mercaptan raise the question whether the corresponding *ortho* and *meta* isomers of this mercapto compound have been correctly described.

<sup>9</sup> Price and Twiss, *J. Chem. Soc.*, 93, 1401 (1908).

<sup>10</sup> Strakosch, *Ber.*, 5, 698 (1872).

<sup>11</sup> O. Fischer, *ibid.*, 28, 1338 (1895).

### Summary.

1. Methyl iodide interacts with the sodium salt of 2-*p*-nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine to give first a nitrogen substituted derivative, which then interacts with another molecule of methyl iodide to form an addition product. The methyl group substitutes in the 1-position of the pyrimidine ring.

2. Ethyl bromide and allyl bromide interact with the mercapto-pyrimidine in a manner entirely different from that with methyl iodide. In both of these cases, an oxygen ether is formed, and no evidence was obtained of substitution of the alkyl groups on a nitrogen atom of the pyrimidine ring.

3. In the hydrolysis of 2-*p*-nitrobenzyl-mercapto-pyrimidines with acids, *p*-nitrobenzyl-mercaptan is formed melting at 57–58°. If, however, free iodine functions during hydrolysis, this mercaptan is destroyed and the disulfide, melting at 126.5°, is formed by oxidation.

4. The literature concerning *p*-nitrobenzyl-mercaptan is incorrect; in this paper the melting points of this compound, its disulfide and corresponding monosulfide are described correctly.

NEW HAVEN, CONNECTICUT.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

## PARA-CYMENE STUDIES. III. THE BROMINATION OF 2-AMINO-PARA-CYMENE.

BY ALVIN S. WHEELER AND IRA W. SMITHEY.<sup>1</sup>

Received August 1, 1921.

The previous two papers dealing with *p*-cymene concerned (1) the production of toluene<sup>2</sup> by the action of aluminum chloride on a mixture of benzene and *p*-cymene and (2) *p*-cymene as a solvent.<sup>3</sup> This paper describes the action of bromine upon 2-amino-*p*-cymene and the preparation of certain derivatives of the monobromo-amino-cymene obtained. The research began with the isolation of cymene from spruce turpentine, a by-product in the manufacture of paper by the sulfite process. In addition to the steps given by one of us in the second paper of this series on the purification of *p*-cymene we find it necessary to shake out the cymene with a limited amount of conc. sulfuric acid. When this is not done the cymene, even though it be a fraction of narrow range in boiling point (176–178°), acquires a yellow color on standing, and fully satisfactory

<sup>1</sup> This paper forms a portion of a thesis submitted by Ira W. Smithey to the faculty of the Graduate School of the University of North Carolina in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> *J. Ind. Eng. Chem.*, 10, 359 (1918).

<sup>3</sup> *THIS JOURNAL*, 42, 1842 (1920).

reactions such as nitration and bromination cannot be carried out with it. Cymene was nitrated by the method of Andrews,<sup>4</sup> modified by the Eastman Kodak Co., who introduce some glacial acetic acid to prevent the product from freezing out. The nitro-cymene was reduced with tin and hydrochloric acid. 2-Amino-*p*-cymene was prepared by Lloyd<sup>5</sup> who heated carvacrol at 350–360° with ammonium bromide and zinc ammonia bromide. Soderbaum and Widman<sup>6</sup> reduced nitrocymene with tin and hydrochloric acid. Goldschmidt<sup>7</sup> treated *isocarvoxime* dissolved in alcohol with zinc dust and acetic acid. Semmler<sup>8</sup> mixed boiling alcoholic solutions of tanacetone-acetoxime and sulfuric acid. Wallach and Schrader<sup>9</sup> heated at 235° carvoxime with conc. aqueous potash. Wallach and Neumann<sup>10</sup> heated *isocarvoxime* with potash at 235°. The method for quantity production is the reduction of nitro-cymene, now that cymene is available in large amounts.

The acetyl derivative of amino-cymene which melts at 71° is smoothly brominated in carbon tetrachloride solution and less satisfactorily in glacial acetic acid solution. Hydrolysis of the brominated product is best effected with conc. hydrochloric acid. The monobromo-amino-cymene thus obtained is a liquid boiling at 169–170° at 20 mm. Its hydrochloride and hydrobromide were prepared.

Considerable effort was made to locate the position of the bromine atom. It did not enter any of the side chains for the product does not possess any properties characteristic of such compounds. The problem was therefore to determine whether it is in Position 3, 5 or 6. The acetyl derivative was oxidized with neutral permanganate and analysis indicated the oxidation of the *isopropyl* group to a carboxyl, forming therefore an acetyl-amino-bromotoluic acid. Hydrolysis gave the hydrochloride of the amino acid and its analysis indicated two acid hydrogens. Finally analysis of the free amino acid agreed with that calculated for a toluic acid. It happens that only one amino-bromotoluic acid is known, the one with bromine at Position 5, melting at 186–187°; whereas our acid melts at 151°. Since an *ortho* compound is far more likely to be formed than a *meta*, we have placed the bromine atoms provisionally at Position 3 and not at 6. We had expected to find it at Position 5. A fuller discussion is reserved for a special part preceding the summary.

Diazo derivatives of amino-bromocymene were prepared by combining it (1) with itself, (2) with aniline and (3) with *p*-nitro-aniline in two

<sup>4</sup> Andrews, *J. Ind. Eng. Chem.*, 10, 453 (1918).

<sup>5</sup> Lloyd, *Ber.*, 20, 1262 (1887).

<sup>6</sup> Soderbaum and Widman, *ibid.*, 21, 2127 (1888).

<sup>7</sup> Goldschmidt, *ibid.*, 26, 2086 (1893).

<sup>8</sup> Semmler, *ibid.*, 25, 3352 (1892).

<sup>9</sup> Wallach and Schrader, *Ann.*, 279, 374 (1894).

<sup>10</sup> Wallach and Neumann, *Ber.*, 28, 1660 (1895).

ways, (a) by diazotizing the amino-bromocymene and (b) by diazotizing the *p*-nitro-aniline. The azo derivatives of *p*-nitro-aniline are yellow and dissolve in alkaline solutions, with the formation of a rich magenta color which disappears on acidification. This marked color change indicates a change of structure and is well explained by a shifting of the hydrogen of the imino group to the nitro group, forming a pseudo acid, the alkaline salt having the group:  $\text{NOONa}$ . Thus:  $\text{C}_3\text{H}_7\text{CH}_2\text{BrC}_6\text{H}_2\text{N}:\text{NNHC}_6\text{H}_4\text{NO}_2 \rightarrow \text{C}_3\text{H}_7\text{CH}_2\text{BrC}_6\text{H}_2\text{N}:\text{NN}:\text{C}_6\text{H}_4\text{NOONa}$ . Meldola<sup>11</sup> noticed the same color change with *p*-dinitro-diazo-amino-benzene but he believed that the sodium atom merely replaced the hydrogen of the imino group. Hewitt and Mitchell<sup>12</sup> proposed the better explanation of a pseudo or nitronic acid where the hydrogen of the imino group wanders to the *para* nitro group. A similar change of structure may be assumed in Grandmougin and Leeman's<sup>13</sup> hexanitro-hydrazo-benzene, the dipotassium salt giving a blue solution.

### Experimental Part.

**Nitration of *p*-cymene.**—The method of Andrews was followed, but some modifications were necessary to obtain good yields. The nitration mixture was placed in an iron kettle of about 12 liters capacity, with a wooden lid provided with holes for stirrer, funnel and thermometer. The kettle was surrounded by ice and salt in a wooden tub of 40 liters capacity. An 18 cm. iron stirrer running at 200–250 r. p. m. was used to agitate the mixture. Two kg. of cymene was nitrated at one time. 2010 g. of cymene, b. p. 176–177°, was added slowly with stirring to 2010 g. of conc. sulfuric acid cooled to 0° or below with ice and salt. The mixture was well stirred to insure the formation of a good emulsion. Andrews calls it a solution but this is impossible, for in our experience it requires a week to dissolve cymene in sulfuric acid and then it is undoubtedly sulfonated. To the ice-cold emulsion a mixture of 1500 g. of conc. nitric acid and 3150 g. of conc. sulfuric acid was added from a dropping funnel at the rate of two drops a second, provided cooling by the freezing mixture was efficient. In order to prevent the freezing out of nitrocymene 300 cc. of glacial acetic acid was added to the cymene-acid mixture at the beginning. The operation of nitration required 15 hours. Stirring was continued for 30 minutes after the last of the acid had been added. The product was poured into 6 liters of water containing ice to keep the temperature below 10°. After thorough stirring the nitro-cymene collected on the surface as a red oil. It was separated, washed with water, very dilute sodium hydroxide (conc. alkali causes a troublesome emulsion), and again with water. It was dried with calcium chloride and distilled. The fraction boiling at 148–162° at 35 mm. represented a fairly pure nitro-cymene. Wheeler and Smith are now engaged in preparing a purer nitro-cymene by preliminary treatment with a small amount of bromine.

**Reduction of Nitro-cymene.**—Nitro-cymene was reduced with tin and hydrochloric acid, the process being the same as that used for nitrobenzene. Instead, however, of distilling the alkaline solution with steam, it was found better to add enough sodium hydroxide nearly to dissolve the tin salt and extract with benzene. After drying the solution with solid sodium hydroxide, the benzene was distilled. 350 g.

<sup>11</sup> Meldola, *J. Chem. Soc.*, 49, 626 (1886).

<sup>12</sup> Hewitt and Mitchell, *J. Chem. Soc.*, 91, 1254 (1907).

<sup>13</sup> Grandmougin and Leeman, *Ber.*, 49, 4384 (1906).

of nitro-cymene gave 260 g. of amino-cymene, the calculated yield being 290 g. A fraction boiling a little below and above  $240^{\circ}$  was used for acetylation with acetic anhydride. The pure acetyl derivative melted at  $71^{\circ}$ .

**2-Acetyl-amino-3-bromo-*p*-cymene**,  $C_9H_7CH_2NHCOCH_3BrC_6H_7$ .—One mol. of acetyl-amino-cymene was dissolved in 5 parts of carbon tetrachloride and treated with one mol. of bromine. The temperature rose to  $50$ – $60^{\circ}$  and considerable hydrogen bromide escaped. When the reaction had proceeded for a short time, a mass of white crystals separated from the solution, forming a seemingly solid mass. These crystals were filtered off and recrystallized from alcohol, forming needles which melted at  $122.5^{\circ}$ . The yield was practically quantitative. Bromo-acetyl-amino-cymene is soluble in ether, alcohol, benzene and acetic acid and insoluble in water. Glacial acetic acid may also be used as a solvent for the reaction but unless the temperature is kept down, some bromine will enter the side chains forming compounds which attack the eyes.

*Analyses.* Subs., 0.1818, 0.2614: AgBr, 0.1250, 0.1805. Calc. for  $C_{12}H_{16}ONBr(270)$ : Br, 29.62. Found: 29.26, 29.38.

A sample of crude acetyl-amino-cymene in carbon tetrachloride was boiled with bromine. A small quantity of greenish material separated from solution. It was recrystallized from alcohol and obtained in golden-yellow leaflets which melted at  $188^{\circ}$ .

**2-Amino-3-bromo-*p*-cymene Hydrochloride**,  $C_9H_7CH_2NH_2(HCl)BrC_6H_7$ .—The acetyl derivative above was so little affected by boiling alcoholic potash even after 6 hours, that hydrolysis was effected by boiling with conc. hydrochloric acid for 1 hour. The action could be hastened by decanting at intervals from the undissolved portion, cooling, filtering off the hydrochloride and returning the acid to the flask. The hydrochloride is almost completely insoluble in cold hydrochloric acid, moderately soluble in ether and very soluble in acetone and acetic acid. It dissolves readily in cold water but is hydrolyzed by hot water. It crystallizes from alcohol in silvery hexagonal plates which melt at  $205$ – $210^{\circ}$  with decomposition.

*Analyses.* Subs., 0.2301, 0.2106: AgCl, 0.1306, 0.1176. Calc. for  $C_{10}H_{14}NBr.HCl(264.5)$ : Cl, 13.41. Found: 14.04, 13.81.

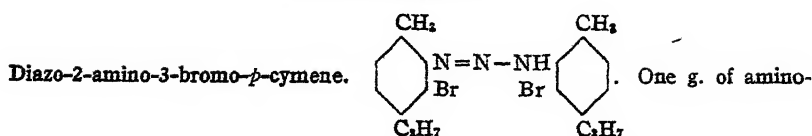
**2-Amino-3-bromo-*p*-cymene Hydrobromide**,  $C_9H_7CH_2NH_2(HBr)BrC_6H_7$ .—Pure amino-bromo-cymene was treated with strong hydrobromic acid. A mass of crystals formed instantly. On recrystallizing from alcohol brilliant octagonal plates were obtained which melted at  $200$ – $205^{\circ}$  with decomposition. This salt is hydrolyzed even by cold water. It is fairly soluble in ether, benzene and acetone.

*Analyses.* Subs., 0.4333, 0.5221: AgBr, 0.2653, 0.3199. Calc. for  $C_{10}H_{14}NBr.HBr(309)$ : Br, 25.88. Found: 26.04, 26.07.

**2-Amino-3-bromo-*p*-cymene**,  $C_9H_7CH_2NH_2BrC_6H_7$ .—Pure amino-bromo-cymene hydrochloride is hydrolyzed with 20% sodium hydroxide and the free amine is distilled with steam. A colorless oil appeared in the upper part of the condenser but it rapidly assumed a yellowish color, being distinctly colored when it dropped from the condenser. The aqueous distillate was saturated with salt and extracted with ether. The ether solution was dried with sticks of sodium hydroxide and the ether was distilled. Pure amino-bromo-cymene was driven over at  $169$ – $170^{\circ}$  under a pressure of 20 mm. It is a colorless oil at first but soon becomes yellow and after some time red like aniline. It is very soluble in ether, alcohol and acids and insoluble in water. Its specific gravity, determined by the pycnometer method at  $21^{\circ}$ , is 1.30125. Its refractive index, determined with an Abbe refractometer at  $20^{\circ}$ , is 1.5781.

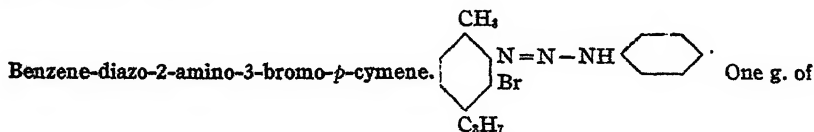
*Analysis.* Subs., 0.2432: AgBr, 0.2005. Calc. for  $C_{10}H_{14}NBr(228)$ : Br, 35.04. Found: 35.08.

## Diazo Derivatives.



bromo-cymene in 10 cc. of water containing 1.5 cc. of conc. hydrochloric acid, cooled to 0°, was treated with 0.4 g. of sodium nitrite in 5 cc. of water. To this solution was added 1 g. of the amine in 5 cc. of water containing 0.5 cc. of conc. hydrochloric acid. The yellow precipitate which formed was more completely precipitated by the addition of 5 g. of sodium acetate dissolved in 5 cc. of water. The product was recrystallized from petroleum ether from which it separated in yellow prismatic needles which melted at 143–146° with decomposition. Yield, 80%. It is slowly soluble in cold ether, glacial acetic acid, benzene and carbon tetrachloride. It is almost insoluble in cold alcohol.

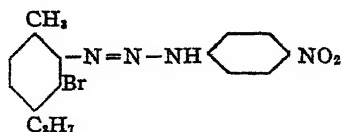
*Analysis.* Subs., 0.1193: AgBr, 0.0966. Calc. for  $C_{20}H_{25}N_3Br_2$  (467): Br, 34.26. Found: 34.45.



amino-bromo-cymene was treated with 10 cc. of water containing 1.5 g. of conc. hydrochloric acid. The mixture was cooled to 0° and a slight excess of sodium nitrite solution was added. Some of the amine salt still remained undissolved. It was stirred for 15 minutes and then a solution of aniline hydrochloride was added. An orange-red precipitate was formed, the precipitation being furthered by the addition of 5 g. of sodium acetate in 5 cc. of water. The salt which separated was very soluble in hot alcohol, benzene and glacial acetic acid, and was best recrystallized from petroleum ether, from which it formed yellow needles melting at 161–162° with decomposition. The salt was hydrolyzed with dil. sodium hydroxide solution. The free amine crystallized in the form of flat yellow needles which melt at 152–154° with decomposition.

*Analysis.* Subs., 0.0960: AgBr, 0.0538. Calc. for  $C_{18}H_{19}N_3Br$ : Br, 24.09. Found: 23.85.

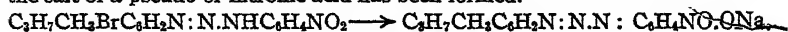
*p*-Nitrobenzene-diazo-2-amino-3-bromo-*p*-cymene. 0.96 g. of amino-bromo-



cymene hydrochloride was dissolved in 2 cc. of conc. hydrochloric acid and 2 cc. of water. On dilution to 40 cc. much of the salt crystallized. The mixture was cooled to 10° and 0.28 g. of sodium nitrite in 5 cc. of water was added all at once and the mixture stirred for 30 minutes. Five-tenths g. of *p*-nitro-aniline was dissolved in 2 cc. of conc. hydrochloric acid and 2 cc. of water, and diluted to 40 cc. The two solutions were mixed and stirred for 30 minutes. The solution was filtered from slight impurities and treated with sodium acetate, whereupon a yellow precipitate was formed. The diazo compound was recrystallized from alcohol and obtained in the form of bright yellow needles which melted at 158° with blackening.

*Analysis.* Subs., 0.0450: AgBr, 0.0228. Calc. for  $C_{16}H_{17}O_2N_4Br$ : Br, 21.22. Found: 21.56.

This bright yellow compound dissolves in ammonium or sodium hydroxide to form a solution with a rich magenta color, and the color disappears on neutralizing or acidifying the solution. If the neutral colorless solution is warmed, the magenta color comes back, though it is then of less intensity. If the solution is cooled with ice the color disappears again. As suggested in the theoretical part of this paper, the marked change of color must be due to a change of structure, the best supposition being that the salt of a pseudo or nitronic acid has been formed.

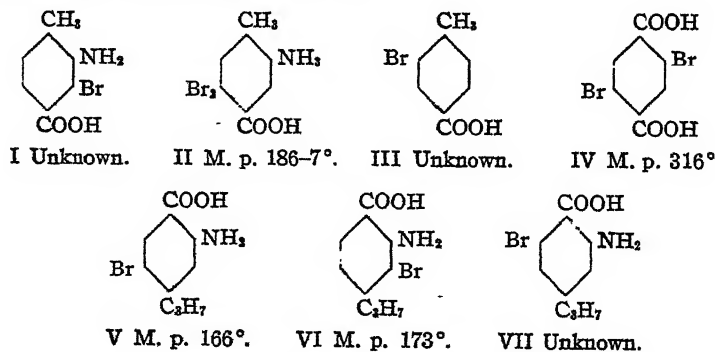


On reversing the process by diazotizing the *p*-nitro-aniline an orange colored precipitate was obtained which was purified by recrystallizing from alcohol. The purified product consisted of orange-red needles with a steel-blue fluorescence, melting at  $163^\circ$  with decomposition. It is soluble in alcohol and benzene. It is soluble in conc. hydrochloric acid and does not readily dissolve in cold aqueous sodium hydroxide. The alkaline solution has a magenta-red color like the other nitro derivative. An analysis could not be made on account of lack of material. We believe that in this compound the azo and imino groups have exchanged places:  $C_6H_7CH_2BrC_6H_2NH.N : NC_6H_4NO_2$ .

#### Orientation of the Bromine Atom.

It seems well established that the amino-*p*-cymene is 2-amino-*p*-cymene. Bromination of its acetyl derivative in the cold introduces one bromine atom. It may occupy any one of 7 positions, 3 of which are in the nucleus and 4 in the side chains, *i. e.*, in the methyl, in the amino and 2 places in the *iso*-propyl group. Positions in the side chains are ruled out on account of the fact that the reaction is carried out at a moderate temperature thus indicating entrance into the nucleus and also since the product has no characteristics of the benzyl bromide type. Again, the side chains may be removed or converted into other radicals while the bromine atom remains unaffected.

The question therefore is whether the bromine is at Position 3, 5 or 6. The best hope of locating it seemed to lie in oxidizing the substance to a toluic acid. Oxidation might however produce a cuminic acid or a terephthalic acid. Of the three possible toluic acids, Formulas I, II and III, only II is known. Only one bromo-terephthalic acid having any bearing on the question is known, the 2,6-dibromo derivative, Formula IV. Two of the three possible cuminic acids, Formulas V, VI and VII, are known, those represented by Formulas V and VI.



Fileti and Crosa<sup>14</sup> having oxidized nitro-bromo-cymene with nitric acid to a toluic

<sup>14</sup> Fileti and Crosa, *Gazz. chim. ital.*, 18, 307 (1888).



acid, we tried nitric acid first. Nitric acid (1:2) converted acetyl-amino-bromo-cymene into an amino acid melting at  $196^{\circ}$ , soluble in acids and alkalies, in ether and benzene and very difficultly soluble in water and ligroin. This substance corresponds to none of the toluic or cuminic acids. Neutral permanganate was then tried.

Two g. of acetyl-amino-bromo-cymene and 4 g. of magnesium sulfate were added to 240 cc. of water, warmed to  $80^{\circ}$ , and 6 g. of powdered potassium permanganate was finally added. Heating was continued for an hour and a half. The manganese dioxide was filtered off, the excess of permanganate destroyed with alcohol, and the colorless filtrate acidified with sulfuric acid. The abundant white precipitate crystallized from dil. alcohol in fine needles which melted at  $215^{\circ}$ . The acidity of the product was determined by titration.

*Analysis.* Subs., 0.1013: KOH (0.05 *N* solution used), 0.02085 g.

Required for acid derivatives: Acetyl-amino-bromo toluic acid,  $C_{10}H_{10}O_2NBr$  (mol. wt. 272): 0.02085 g. Acetyl-amino-bromo-cuminic acid,  $C_{12}H_{14}O_2NBr$  (mol. wt.) 300): 0.01890 g. Acetyl-amino-bromo-terephthalic acid,  $C_{10}H_8O_4NBr$  (mol. wt. 302): 0.03753 g.

The product is therefore a toluic acid. It was then hydrolyzed, 0.5 g. being boiled for 30 minutes with 40 cc. of conc. hydrochloric acid. The hydrochloride crystallized in leaf-like crystals which melted at  $190^{\circ}$  with decomposition.

*Analysis.* Subs., 0.1054: KOH, 0.0419 g. Required for 2 acid hydrogens: 0.0427.

The analysis gives indication of a toluic acid. The substance was finally saponified with sodium hydroxide. From the solution acidified with acetic acid a white precipitate separated which turned pinkish after a time. It crystallized from dilute alcohol in yellowish needles which melted at  $151^{\circ}$ .

*Analysis.* Subs., 0.1022: KOH, 0.0247 g. Required for the 3 possible acids: Amino-bromo-toluic acid,  $C_8H_9O_2NBr$  (mol. wt. 230): 0.0248 g. Amino-bromo-cuminic acid,  $C_{10}H_{11}O_2NBr$ , (mol. wt. 258): 0.0221 g. Amino-bromo-terephthalic acid,  $C_8H_7O_4NBr$  (mol. wt. 280): 0.0440 g.

A toluic acid is again indicated. The 3 analyses point to a toluic acid of molecular weight of 272. We had expected to obtain toluic acid II with bromine in Position 5, but the acid melts at  $151^{\circ}$  instead of  $186-187^{\circ}$ . In choosing I instead of III, we are guided by the fact that the bromination of other amino compounds yields *ortho* and *para* compounds and not *meta*. The bromination of 4-amino-*m*-xylene<sup>15</sup> puts bromine *ortho* to the amino group. In this case the *para* place is already occupied. The bromination of 2-amino-*p*-xylene<sup>16</sup> puts bromine *para* to the amino group. Fischer and Windhaus<sup>16</sup> did not however prove it, merely stating that it was "wahrscheinlich." Everything considered we believe that the location of the bromine atom at Position 3 should be regarded as provisional.

### Summary.

1. The nitration of *p*-cymene is described and the reduction of 2-nitro-*p*-cymene.
2. The bromination of 2-amino-*p*-cymene yields the new compound, 2-amino-3-bromo-*p*-cymene. Its acetyl derivative, hydrochloride and hydrobromide are described.
3. Diazo derivatives were prepared, including the coupling of amino-

<sup>15</sup> Noelting, Braun and Thesmar, *Ber.*, 34, 2255 (1901).

<sup>16</sup> Fischer and Windhaus, *ibid.*, 33, 1974 (1900).

bromo-cymene with (1) itself, (2) aniline and (3) *p*-nitro-aniline in two ways.

4. Conversion of the amino-bromo-cymene into a hitherto unknown amino-bromo-toluic acid suggests that the bromine atom occupies Position 3.

5. A new toluic acid, 2-amino-3-bromo-*p*-toluic acid, was prepared; also its hydrochloride and acetyl derivative.

CHAPEL HILL, NORTH CAROLINA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

## SOME COMPOUNDS OF PIPERIDINE WITH HALIDES.

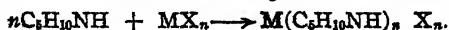
By CLIFFORD S. LEONARD.

Received August 4, 1921.

### I. Inorganic Halides.<sup>1</sup>

A series of new halide compounds may be prepared from piperidine by reaction with halides of trivalent arsenic, antimony, and phosphorus and of tetravalent silicon, tin, and titanium. The solvent used is normal heptane. The complete miscibility of most of the halides employed and of the piperidine with heptane, together with the inert nature of the latter, favor its use. In each case the reaction takes place with as many piperidine molecules as there are halogen atoms available (with the exception of tin chloride, of which two chlorine atoms are inactive).

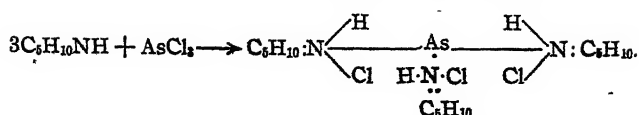
The reaction appears to be an addition like the formation of ammonium halides from ammonia and hydrogen halides. In general, if *M* is the metalloid, *n* its valence and *X* the halogen, the reaction may be written



The behaviors of the complexes formed are like those of ammonium compounds, *i. e.*, they appear to be piperidinium compounds. We may write the equation and the structural formula in the following way, taking  $AsCl_3$  as the example:<sup>2</sup>

<sup>1</sup> This work comprises part of a thesis presented in June, 1920, to the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. See the preliminary note, read by Prof. Edward Kremers before the American Chemical Society, in *Science*, 53, 145 (1920). The formula given in this note is incorrect; a typographical error adds an extra arsenic atom.

<sup>2</sup> Whether the mechanism is direct addition or a substitution followed by addition of freed HCl does not matter as to resultant product. It has been the habit to beg the question of the nature of organic amino-halides; thus aniline and HCl give aniline "hydrochloride." Since this work was completed, Schmidt at the University of Wisconsin has studied similar products from  $AsCl_3$  and aniline. He has named them as substituted aniline hydrochlorides, as is conventional. Obviously their nature must be similar, however, to the compounds here described. (See Schmidt, *This Journal*, 43, 2449 (1921).)



With tetravalent elements such as silicon the fourth halogen carries a fourth imino nitrogen to pentavalence in the same way. These salts may be expected to resemble any known addition products of ammonia itself to the various halides used. Such is borne out by the case of tin tetrachloride. This is described<sup>3</sup> as forming a complex with 2 mols of ammonia instead of 4 as might be expected. The complex with 4 mols is known but is much less stable than the one with 2 mols. So, with piperidine, the complex with tin tetrachloride, which forms even though 4 mols of piperidine are supplied, is the dipiperidyl compound.

If the above is the correct structure, complexes of the following formulas have been studied. (1)  $(\text{C}_6\text{H}_{10}\text{N} \cdot \text{HCl})_3\text{As}$ , which, if named in accordance with the organic "piperidinium" compound described below, is: arsine-tri-1-piperidinium chloride; (2)  $(\text{C}_6\text{H}_{10}\text{N} \cdot \text{HCl})_3\text{Sb}$ , stibine-tri-1-piperidinium chloride; (3)  $(\text{C}_6\text{H}_{10}\text{N} \cdot \text{HCl})_4\text{Si}$ , silicane-tetra-1-piperidinium chloride; (4)  $(\text{C}_6\text{H}_{10}\text{N} \cdot \text{HCl})_2\text{SnCl}_2$ , dichlorostannane-di-1-piperidinium chloride; (5)  $(\text{C}_6\text{H}_{10}\text{N} \cdot \text{HCl})_4\text{Ti}$ , titanane-tetra-1-piperidinium chloride. The phosphorus complex was too unstable for accurate analysis, but qualitative tests show the presence of both phosphorus and chlorine as well as piperidine, and if it is analogous to the arsenic salt it is (6)  $(\text{C}_6\text{H}_{10}\text{N} \cdot \text{HCl})_3\text{P}$ , phosphine-tri-1-piperidinium chloride. It is possible that similar compounds will form with the same readiness from lead tetrachloride, boron trichloride, germanium tetrachloride and vanadium tetrachloride, providing these are soluble in the heptane. These chlorides were not available for the present investigation.

Many halide compounds of piperidine have been prepared but none from these liquid halides of Groups IV and V. The compounds previously made have always been labeled as double salts. The writer believes that those which are made from *piperidine base* and a metallic or non-metallic halide may be likened to ammonium salts and named piperidinium compounds. The simplest would be exact analogs of ammonium chloride; thus, piperidine hydrochloride,  $\text{C}_6\text{H}_{10}\text{NH} \cdot \text{HCl}$ , probably is piperidinium chloride.

Here it may be noted that another type of complex may be formed from these piperidinium salts by further addition, just as double salts may be made from ammonium salts. In the literature this latter type has never been distinguished from the former simpler type. The simpler group will be designated in this paper as Type I, resulting from the combination of piperidine base with metal, metalloid or hydrogen halide. Its prototype

<sup>3</sup> H. Davy, *Schweigger's J. Chem. Physik.*, 10, 321 (1814).

is ammonium chloride,  $\text{NH}_4\text{Cl}$  (Werner's primary compounds). The other group, Type II, is formed from compounds of Type I by addition of another halide. Its prototype is ammonium zinc chloride,  $2\text{NH}_4\text{Cl} \cdot \text{ZnCl}_2$ , ammonium halide double salts (Werner's secondary compounds).

For Type I only the ordinary pentavalence of nitrogen need be invoked while Type II requires extra or subsidiary valences of either nitrogen or halogen to explain its structure. The writer does not intend to go into a discussion here of the valence difference between compounds such as represented by the formulas  $\text{NH}_4\text{Cl}$  and  $2\text{NH}_4\text{Cl} \cdot \text{ZnCl}_2$ . Whatever that is found to be, under Werner's theory or any other theory the same difference will hold between piperidinium salts and piperidinium salt addition compounds.<sup>4</sup>

As an example of Type II may be taken the complex formed from platinous chloride and piperidine hydrochloride and named by Cahours, piperidine chloroplatinate,  $\text{C}_5\text{H}_{10}\text{NH} \cdot \text{HCl} \cdot \text{PtCl}_2$ .<sup>5</sup> If he had taken, as did Williams<sup>6</sup> later, piperidine base and platinous chloride he would have obtained the Type I compound,  $\text{C}_5\text{H}_{10}\text{NH} \cdot \text{PtCl}_2$ . For the sake of brevity a list of piperidine halide compounds in which Type I has been separated from Type II is given at the end of this paper.

The new compounds are of surprisingly high stability. All but the antimony and the phosphorus complexes (the latter was unstable and deliquesced in the air) can be recrystallized from alcohol. The arsenic compound can be recrystallized from water and the hot solution even clarified with bone charcoal. It gives a neutral water solution.<sup>7</sup> The tin and silicon compounds can be recrystallized from alcohol but tend to hydrolyze in the presence of water to form the hydroxides. Addition of dilute alkalis precipitates tin and silicon more completely. The antimony complex is hydrolyzed by 99% alcohol, freeing piperidine hydrochloride.

Confirmation of the belief that these complexes are related to ammonium chloride is afforded by the fact that they themselves further add metal salts as does ammonium chloride. Thus this salt yields with the highly colored lead di-iodide a nearly colorless addition compound (Type II). In an analogous manner the piperidine-arsenic compound has been found to give a crystalline addition complex with lead di-iodide. It reacts similarly with mercuric iodide giving a pale yellow-green compound, which is very different from either yellow or red iodide of mercury. So, too, does arsenious iodide lose its orange color and give a white, crystalline

<sup>4</sup> The newer octet atom-structure theories provide for Type I, *i. e.*, for  $\text{NH}_4\text{Cl}$ . Probably further development of these theories in connection with crystal-structure work will throw light on the Type II structure. See papers by Langmuir and Sir J. J. Thompson.

<sup>5</sup> Cahours, *Ann. chim. phys.*, 38, [III] 78 (1853).

<sup>6</sup> Williams, *Chem. Gaz.*, 1858, p. 346; *J. prakt. Chem.*, 76, 251 (1859).

<sup>7</sup> Conductivity determinations to show the type of ion present would be of interest.

addition product with the piperidine-arsenic compound. The Type I complex adds halides to form products of Type II.

Much difficulty was experienced in the analysis of the new compounds, as might be expected from the presence together of imino nitrogen, chlorine, metalloid, carbon and hydrogen. Arsenic was determined by Ewins' method.<sup>8</sup> Chlorine was determined by the Stephanoff-Bacon<sup>9</sup> method and gave good checked results. Carbon, however, could not be determined by total combustion. Possibly a combustion in the wet way would have succeeded, but a quicker method of analysis was devised as described below.

It was found that the compounds could be hydrolyzed with dilute alkali and the freed piperidine base distilled into standard acid. The acid could be titrated back against standard alkali, and the percentage of piperidine calculated. This method had the further advantage that chlorine could be determined in the distillation residues by simply acidifying with nitric acid and determining by the Volhard method. These latter chlorine determinations checked well with the determinations by the previously cited method. Results checked well in the case of the arsenic compound, so the piperidine and chlorine determinations were considered sufficient to identify the remaining complexes.

The arsenic compound was studied most carefully because of its possible value in medicine. No previously described arsenical compound has been investigated pharmacologically in which the arsenic is bound to the nitrogen of a heterocyclic ring.<sup>10</sup> The findings regarding pharmacological properties of the arsenic compound will be published elsewhere.

### Experimental.

**The Solvent.**—The solvent used in all these experiments was a purified normal heptane obtained from the oil of Jeffery pine. Purification was by the hydrochloric acid method of Sherck;<sup>11</sup> after drying over sodium, the heptane boiled between 97° and 98°. With these very reactive liquid halides the solvent must be dry and free from terpenes or other impurities. Fractions of heptane containing pinene give with arsenic trichloride a brown resin, very slowly precipitated on the wall<sub>15</sub> of the vessel. Even with pure solvent some of the halides react to a slight extent. Clear solutions were obtained with arsenic, silicon, and phosphorus halides. Tin and titanium tetrachlorides gave small amounts of red-brown flocculent pre-

<sup>8</sup> Ewins, *J. Chem. Soc.*, 109, 1356 (1916).

<sup>9</sup> Stephanoff, *Ber.*, 39, 4056 (1906). Bacon, *THIS JOURNAL*, 31, 49 (1909).

<sup>10</sup> One piperidine complex containing arsenic has recently been made by Jacobs and Heidelberger, (*THIS JOURNAL*, 41, 1593 (1919)), N-phenyl-4-arsenic-glycine piperidide, but the piperidine group is not attached to arsenic and the arsenic is in the oxidized form of an arsonic acid.

<sup>11</sup> Sherck, *J. Am. Pharm. Assoc.*, 9, No. 11, 1 (1921).

precipitate from which the clear solution could be decanted. Antimony trichloride (crystalline) reacts immediately with heptane to form a gummy red-brown resin. This tends to coat the crystals and prevent further solution. The antimony trichloride was shaken with solvent for from 12 to 24 hours; then the resin was allowed to settle and the clear solution decanted off.

**General Procedure in the Preparation of the Compounds.**—The halide was weighed out and diluted with solvent to a definite volume. Thus each cubic centimeter contained a known weight of halide. The piperidine was similarly prepared. Piperidine solution was then measured into the reaction vessel which was cooled with ice when a large quantity was employed, and the measured volume of halide solution was slowly poured in with stirring. Immediate precipitation occurred. Stirring was continued for some time, then the solution was allowed to stand and was warmed to room temperature. Refluxing at the boiling point of the heptane was not found to change the character of the material. As the precipitates were very voluminous and held much heptane either by capillarity or by adsorption, the reaction mass was usually a light yellow or white mud. The material was filtered and pressed. The precipitates were found to dry thoroughly with little decomposition on standing in the air. Final drying before analysis was in a desiccator over calcium chloride. No hydrochloric acid is given off at any stage of the preparation, which is evidence in itself that the reaction is an addition. The piperidine was commercial material. The halides were the purest obtainable reagents.

**Arsenic Compound,  $(C_6H_{10}N.HCl)_3As$ .**—By the above method arsenic trichloride was combined with piperidine. Preliminary experiments showed that the same white compound formed whether 1, 2 or 3 mols of piperidine were present, only in different amount. In the single case of this arsenic complex the heptane holds about  $\frac{1}{3}$  of the material in solution. This could be precipitated by adding an equal volume of ether. The total yield then approximated that calculated. The arsenic compound could be recrystallized from alcohol in long needles, nearly pure white in color, melting at  $238^\circ$ .

The compound was very soluble in water (about 1:1). On evaporating a water solution to dryness, no change of weight of arsenic compound was found to have occurred. Consequently the material was crystallized from water thereafter. Long heating in water caused the solution to darken in color. Such solutions could be boiled with bone charcoal, then filtered and would come through light yellow in color. In this way excellent crops were obtained, melting at  $240^\circ$ . Whether recrystallization was from alcohol or water, on redissolving the substance after air drying, small amounts of white, insoluble material were always present. Possibly, therefore, there is a slight hydrolysis or oxidation of the complex in the air.

The arsenic compound was soluble in chloroform, pyridine and carbon disulfide; somewhat soluble in heptane, insoluble in ether, petroleum ether, acetone and carbon tetrachloride.

Piperidine was determined by the distillation method described above. A Volhard chlorine determination was run on the distillation residue. Ewins' iodometric method was used for arsenic.

*Analyses.* Calc. for  $(C_5H_{10}N.HCl)_3As$ : piperidine, 58.4; Cl, 24.35; As, 17.20. Found: piperidine, 62.1; Cl, 24.78; As, 13.09; total, 99.97.

This was further checked by Dumas nitrogen determinations and by chlorine determinations by the Stephanoff-Bacon method. Although total combustions were not successful in determination of carbon, the water, and consequently the hydrogen from these checked well, and averaged very close to the calculated results. When carbon is calculated from the piperidine figure above and the other percentages are all taken from direct determinations, the following are the results.

*Analyses.* Calc.: C, 41.16; H, 7.67; N, 9.62; Cl, 24.35; As, 17.20. Found: C (from piperidine), 43.8; H (comb.), 7.92; N (Dumas), 11.17; Cl (Bacon), 24.78; As (Ewins), 13.09; total, 100.76.

Piperidine results are a little higher than the calculated and arsenic low by about the same amount.<sup>12</sup>

*Addition reactions* of the arsenic compound. Just as ammonium chloride and lead di-iodide give a white, crystalline addition product,<sup>13</sup> so the arsenic compound and colored halides react. *With lead iodide.* One g. of orange-yellow lead di-iodide was triturated with 2 g. of the arsenic compound and with 1 cc. of water. The reaction did not go to completion until the mixture was heated to boiling, but then the solution had a faint yellow color, and pale yellow needle crystals of a complex formed on cooling. The solution could be diluted to 15 cc. without decomposition and with the same crystals re-appearing after each heating and cooling. *With mercuric iodide.* One g. of red mercuric iodide was similarly triturated with the arsenic compound and on boiling gave a green solution. When cooled, pale yellow-green needle crystals formed of different color from crystals of yellow mercuric iodide. The solution could be diluted to about 5 cc. without change, but beyond this dilution red mercuric iodide precipitated and on heating, collected as yellow liquid on the bottom, solidifying as yellow mercuric iodide on cooling, and gradually changing to the red form. *With arsenic iodide.* One g. of arsenic tri-iodide was similarly triturated with the arsenic compound and while a clear solution was not obtained as in the previous cases, on heating to boiling, then cooling, rose colored to white crystals formed above the permanent precipitate (the latter probably from impurities in the tri-iodide used). On dilution to 5 cc. this white complex continued to come out on cooling after short boiling. With great dilution it did not appear, but the deep orange color of arsenic tri-iodide did not reappear.

The arsine-tri-1-piperidinium chloride does not give a precipitate with the general alkaloidal reagents except with phosphomolybdic acid, when the precipitate is of light yellow color.

*Antimony Compound,  $(C_5H_{10}N.HCl)_3Sb$ .*—Antimony trichloride dissolved in heptane (see difficulty under "solvent") was added to piperidine solution in the ratio of one mol to three. The white solid which precipitated had a melting point of 235° after air-drying. The white precipitate was recrystallized from 99% alcohol. The recrystallized product, however, analyzed not as the antimony complex expected but as piperidine hydrochloride with just enough antimony to give a qualitative test.

*Analyses.* (Recrystallized material). Calc. for  $(C_5H_{10}N.HCl)_3Sb$ : piperidine, 52.99; Cl, 22.07. Calc. for  $C_5H_{10}N.HCl_3$ : piperidine, 70.06; Cl, 29.1. Found: piperidine, 68.14; Cl, 29.47.

On analysis, the unrecrystallized material was found to approach the formula which had been expected.

<sup>12</sup> Schmidt (Ref. 2) discards Ewins' method for arsenic, as giving low results for the aniline-arsenic-chloride compound.

<sup>13</sup> "U. S. Pharmacopeia," VIII, p. 309 (1890).

Calc. for  $(C_5H_{10}N.HCl)_3Sb$ : piperidine, 52.99; Cl, 22.07. Found: piperidine, 49.81; Cl, 21.85.

**Silicon compound**,  $(C_5H_{10}N.HCl)_4Si$ .—This was prepared in the same manner as the arsenic compound but using 4 mols of piperidine to each mol of silicon tetrachloride. The melting point of the product recrystallized from 99% alcohol was  $238^\circ$ . The substance was also soluble in chloroform. A small amount of flocculent precipitate filtered from the alcohol solution, was dried and found to be wholly inorganic. Probably the percentage of water in the alcohol hydrolyzed a little of the compound to silicic acid. Possibly it may have come from oxychloride in the reagent, however.

*Analyses.* Calc. for  $(C_5H_{10}N.HCl)_4Si$ : piperidine, 66.66; Cl, 27.78. Found: piperidine, 65.97; Cl, 28.18.

**Tin Compound**,  $(C_5H_{10}N.HCl)_2SnCl_2$ .—Prepared by the general method from 4 mols of piperidine and 1 mol of tin tetrachloride. The white precipitate was recrystallized from alcohol, and melted at  $201^\circ$ . (On adding more stannic chloride to the heptane mother liquor a further precipitate of the material was obtained, indicating the presence of excess of piperidine). The tin compound did not analyze for  $(C_5H_{10}N.HCl)_4Sn$  as had been expected in analogy with the arsenic and silicon compounds. It was found to approximate to  $(C_5H_{10}N.HCl)_2SnCl_2$ .

*Analyses.* Calc. for  $(C_5H_{10}N.HCl)_4Sn$ : piperidine, 56.64; Cl, 23.6. Calc. for  $(C_5H_{10}N.HCl)_2SnCl_2$ : piperidine, 39.54; Cl, 32.91. Found: piperidine, 36.51; Cl, 36.17.

Chlorine is thus present in greater amount, and piperidine in less amount, than calculated for the di-piperidyl compound.

**Titanium compound**,  $(C_5H_{10}N.HCl)_4Ti$  (?).—Only a small amount of titanium tetrachloride was available for this work. On mixing 1 mol with 4 mols of piperidine in heptane a leaf-green precipitate formed. This was filtered on a Büchner funnel but began to lose color as it dried. Within a few minutes it had become white. The melting point was  $238-240^\circ$ . On analysis of the unrecrystallized product, the result for piperidine was found to be quite low for the formula  $(C_5H_{10}N.HCl)_4Ti$ , and nearer in fact to that for  $(C_5H_{10}N.HCl)_2TiCl_2$ . However, the chlorine result was nearer that calculated for the first formula and much lower than for either dipiperidyl or tri-piperidyl complexes.

*Analyses.* Calc. for  $(C_5H_{10}N.HCl)_4Ti$ : piperidine, 64.21; Cl, 26.73. Calc. for  $(C_5H_{10}N.HCl)_2TiCl_2$ : piperidine, 47.38; Cl, 39.37. Found: piperidine, 51.68; Cl, 24.83.

Probably the unrecrystallized material as analyzed was more or less a mixture, but more titanium tetrachloride was not available, so that this could not be determined.

**Phosphorus compound**,  $(C_5H_{10}N.HCl)_3P$  (?).—Phosphorus trichloride was found to give a white precipitate with 3 mols of piperidine. No hydrogen chloride came off in this reaction. The precipitate on filtering was found to be very susceptible to the moisture of the air, turning yellow and gummy. It was dried in a vacuum desiccator but had then deteriorated too much for analysis. Qualitative tests showed the presence of both phosphorus and chlorine. If the analogy with the other compounds holds the formula should be  $(C_5H_{10}N.HCl)_3P$ . Michaelis and Luxembourg<sup>14</sup> prepared in ether solution a substance of the formula  $(C_5H_{10}N)_3P$ , but this was by precipitating in the presence of a large excess of piperidine. Probably the addition of 3 mols' excess of piperidine would convert the hydrochloride into the free phosphine by virtue of the stronger basicity of piperidine. The phosphorus compound may be worthy of further investigation.

<sup>14</sup> Michaelis and Luxembourg, *Ber.*, 28, 2207 (1895).



II. 1-( $\alpha$ -methylamyl)piperidinium-iodide.

It was thought that piperidine should give addition compounds similar to those with inorganic halides described above, by reaction with organic halides of longer chain than the simpler carbon halides, carbon tetrabromide, and acetylene iodide, etc., which Dehn<sup>15</sup> had investigated.  $\alpha$ -Methylamyl-iodide, being at hand, was tried.

The halide freshly distilled was mixed with a heptane solution containing one mol of piperidine. The mixture was refluxed for one hour. White crystals began to appear at the edge of the liquid and later a red oil was seen on the bottom. On cooling the mixture and shaking, the red oil crystallized to yellow needles. These were filtered out and dried. The yield was about  $1/3$  that calculated for the monopiperidyl complex. The mother liquor was distilled and could be separated into a fraction containing heptane and piperidine, and a fraction containing  $\alpha$ -methylamyl iodide. On remixing these and after standing, more of the yellow crystals appeared. Possibly, therefore, longer refluxing would have increased the original yield. The  $\alpha$ -methylamyl iodide compound was very soluble in alcohol and in water. The melting point was unchanged after recrystallization with alcohol, 133°. The substance was also soluble in chloroform and slightly soluble in ether, insoluble in heptane, carbon tetrachloride or carbon disulfide.

Analysis by the piperidine distillation method described in the previous paper showed it to be a substance of the formula  $(C_5H_{10}N.HI)C_6H_{12}$ .

Analyses. Calc.: piperidine, 28.18; I, 42.71. Found: piperidine, 29.01; I, 43.15.

If the structure of this compound is to be explained on the same basis as that of the metalloid compounds, it is a *sec*-hexyl-piperidonium iodide  $(C_5H_{10}N(HI)-CH(CH_3).CH_2CH_2CH_2CH_3)$ . This reaction opens up possibilities in the coupling of organic halides and organic bases in heptane solution. If other aliphatic monohalides give similar addition products with piperidine, and these have sharply defined melting points, these may be useful in identification of the different aliphatic halides. There are further possibilities of preparation of various organic compounds from these piperidinium halides, for instance, by replacement of the halogen. The results of Grignard reactions might be interesting if this treatment were found not to decompose the original complex.

## Summary.

A series of new addition compounds of piperidine with halides of elements of the fourth and fifth group of the periodic system have been prepared. They comprise substances of the following formulas:  $(C_5H_{10}N.HCl)_3As$ ,  $(C_5H_{10}N.HCl)_3Sb$ ,  $(C_5H_{10}N.HCl)_4Si$ ,  $(C_5H_{10}N.HCl)_2SnCl_2$ , and titanium and phosphorus compounds which are probably of similar structure.

Reasons are advanced for assigning to these the structure of piperidinium chlorides, and known piperidine addition compounds are assigned to two groups, according to whether they are (Type I) compounds of piperidine free base and a halide or acid or salt, or (Type II) compounds of piperidine hydrohalides with halides.<sup>16</sup>

<sup>15</sup> Dehn, THIS JOURNAL, 34, 286 (1913); 33, 1588 (1912).

<sup>16</sup> Piperidine addition compounds. Type I, with AgBr, AgI, AgCl, HgCl<sub>2</sub>, HgBr<sub>2</sub>, HgI<sub>2</sub>, ZnCl<sub>2</sub>, CdCl<sub>2</sub>, CdBr<sub>2</sub>, CdI<sub>2</sub>, CBr<sub>4</sub>, Cl<sub>3</sub>H, C<sub>2</sub>I<sub>4</sub>, PtCl<sub>2</sub>, PdCl<sub>2</sub>, AgCN, CuSO<sub>4</sub>, HgSO<sub>4</sub>, Hg(CN)<sub>2</sub>, H<sub>4</sub>FeCN<sub>6</sub>, H<sub>3</sub>FeCN<sub>6</sub>, H<sub>3</sub>CoCN<sub>6</sub>. See Beilstein, "Handbuch der Organischen Chemie," Voss, etc.

Type II, the proper hydrohalide of piperidine with AuCl<sub>3</sub>, AuBr<sub>3</sub>, AgBr, AgCl, AgI, HgBr<sub>2</sub>, TiCl<sub>3</sub>, BiI<sub>3</sub>, SeBr<sub>4</sub>, PtCl<sub>3</sub>.

$\alpha$ -Methylamyl iodide with piperidine in heptane forms a crystalline  $\alpha$ -methylamyl-piperidinium-iodide. This is considered to be analogous in structure to the piperidine-metalloid compounds described above.

Thanks are due to Professor Edward Kremers for guidance in this investigation.

MADISON, WISCONSIN.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

### TETRAPROPYL-ETHANE.

BY JEAN PICCARD AND RAY Q. BREWSTER.<sup>1</sup>

Received August 9, 1921.

The number of heavier hydrocarbons with side-chained structures described in the literature is very small. Yet these hydrocarbons are of interest not only to the physical chemist in view of their surface tension and other constants, but also to the organic chemist for the identification of the carbon skeleton of unknown compounds. While in recent years many new methods have been found for the determination of characteristic groups in organic molecules, practically no progress has been made toward the determination of the carbon skeleton since Baeyer's distillation with zinc dust and its famous application to the identification of alizarin. So many good reducing agents have been found in the last few years, however, that it should be possible in most cases to reduce, in well defined successive steps, any organic compound to the corresponding saturated hydrocarbon.

Several years ago Baeyer and Piccard,<sup>2</sup> while working on dimethylpyrone, discovered an interesting violet dye of unknown constitution. The identification of its carbon skeleton was attempted by the oxidation methods in general use. A considerable number of new derivatives were thereby obtained without any progress toward the solution of the problem, since all the oxidation products obtained were unknown.

The problem was later attacked by Piccard and Edmond Wallach and still later by Piccard and McLauren, who applied successively different reduction methods with the purpose of obtaining a saturated hydrocarbon. Unfortunately this work was twice interrupted by the military obligations of the collaborators. Since there are reasons for believing that the hydrocarbon which would result from complete reduction of the violet dye would be symmetrical tetrapropyl-ethane, and since this hydrocarbon is not yet described in the chemical literature, the present work was begun parallel to the work of our collaborators Wallach and McLauren, with the

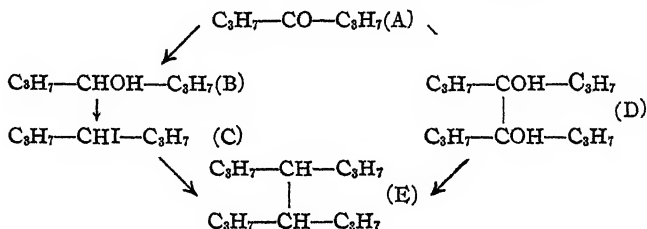
<sup>1</sup> The material presented here is used by Ray Q. Brewster in his dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

<sup>2</sup> Baeyer and Piccards, *Ann.*, **384**, 208 (1911); **408**, 332 (1915).

purpose of synthesizing the new hydrocarbon by the Wurtz reaction. Since the reduction of the violet dye has thus been indefinitely delayed this synthesis of tetrapropyl-ethane is now published separately.

### The Synthesis of Sym. Tetrapropyl-ethane.

The plan of the work was as follows. Butyrene (A) obtained by the dry distillation of calcium butyrate, was reduced by means of metallic sodium and a little water, forming as the chief product  $\delta$ -oxyheptane (B) and a smaller quantity of the pinacone, tetrapropyl-glycol (C). The  $\delta$ -oxyheptane (dipropyl-carbinol) was transformed into its iodide<sup>3</sup> (D) which, when boiled with sodium in ether solution, gave the desired hydrocarbon, tetrapropyl-ethane, (E). However, the fact that the Wurtz reaction is sometimes liable to proceed with rearrangements led us to look for another method for the synthesis of the tetrapropyl-ethane. For this purpose the reduction of the symmetrical tetrapropyl-glycol was selected.



The reduction of the pinacone was a difficult piece of work but there was finally obtained a pure hydrocarbon in quantities sufficient for comparison with the hydrocarbon first prepared from the  $\delta$ -heptyl iodide. Both compounds were found to be identical. Hence the new tetradecane is the desired *sym.* tetrapropyl-ethane or bis- $\delta$ -heptyl.

### Experimental Part.

Butyrene was prepared by the distillation of calcium butyrate. In the first experiments the calcium butyrate, in 200 to 300g. lots, was distilled from a large copper tube heated in a combustion furnace. However, there was some difficulty with the tube becoming clogged; and the yield of the butyrene was not so large as when the calcium butyrate was distilled in smaller portions. This observation is in agreement with the experiments of Chancel.<sup>4</sup>

In the method finally adopted the calcium butyrate was distilled from a 500cc. copper flask in portions of 50 g. each. Before beginning the operation the air was swept out of the flask by a stream of carbon dioxide. The carbon dioxide was then shut off and the flask heated with the full heat of one Bunsen burner. At the end of the process the volatile products remaining in the flask were carried over into the condenser by a stream of carbon dioxide. The average yield was about 26 cc. of crude butyrene

<sup>3</sup> Friedel, *Jahresber.*, 1869, 514.

Kurtz, *Ann.*, 161, 214 (1872).

<sup>4</sup> Chancel, *Ann.*, 52, 295 (1844).

with 2.5-3.0 cc. of water. The time used for the complete operation was about 25 minutes.

The crude butyrone (465 cc.) was subjected to a steam distillation, dried and fractionated. The fraction boiling at 140-146° was collected. Yield, 200, g. The moistened butyrone was reduced to dipropyl-carbinol and tetrapropyl-glycol by means of metallic sodium.<sup>5</sup> In order to increase the relative yield of the pinacone the butyrone was diluted with as little ether as possible. From 120 g. of butyrone there was obtained 84 g. of  $\delta$ -oxyheptane and 23.5 g. of the tetrapropyl-glycol, boiling at 150° and 260° respectively. The latter solidified in the receiver, and after recrystallization from ether melted at 68°.

$\delta$ -Heptyl iodide,  $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CHI}$ .—Fifty g. of  $\delta$ -oxyheptane (dipropyl-carbinol) was mixed with 10 g. of red phosphorus and to this was added 60 g. of iodine in small portions. After 3 hours the reaction product was washed with dil. sodium hydroxide solution, dried and distilled. It passed over with partial decomposition at 180-185°. Distillation under reduced pressure gave the heptyl iodide in almost colorless form. It distills at 65-67° under 9 mm. pressure with only very slight decomposition.<sup>6</sup>

*Analyses.* Subs., 0.1322, 0.2245: AgI, 0.1363, 0.2323. Calc. for  $\text{C}_7\text{H}_{15}\text{I}$ : I, 56.19. Found: 55.73, 55.93.

*Sym. Tetrapropyl-ethane*,  $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CHCH}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$ .—For the preparation of symmetrical tetrapropyl-ethane by the Wurtz reaction, 58 g. of  $\delta$ -heptyl iodide was dissolved in 150 cc. of absolute ether. Twenty g. of sodium wire was added and the solution was boiled for 20 hours. The ether solution was then separated from the sodium iodide and unchanged sodium, washed with water and dried. After removal of the ether the remaining oil was fractionated. The first portion of the distillate consisted of 8 cc. of a hydrocarbon boiling at 98-100° which undoubtedly was *n*-heptane. The main fraction distilled at 215-225° and was considered to be the desired tetrapropyl-ethane. After purification with conc. sulfuric acid and redistillation the product gave the boiling points 220° at 760 mm. and 105-106° at 12 mm. It was halogen-free (copper oxide test), and the pink coloration produced by a trace of iodine showed that it was also free from oxygen. The liquid is remarkably thin for a hydrocarbon of such a high molecular weight. This low viscosity is due to the fact that the molecule contains two side chains. On cooling with solid carbon dioxide and ether the oil became extremely viscous but did not crystallize.

The combustion was made in an atmosphere of nitrogen.

*Analyses.* Subs., 0.1200, 0.1383:  $\text{CO}_2$ , 0.3730, 0.4297;  $\text{H}_2\text{O}$ , 0.1630, 0.1912. Calc. for  $\text{C}_{14}\text{H}_{30}$ : C, 84.75; H, 15.25. Found: C, 84.77, 84.74; H, 15.20, 15.47.

The molecular weight was measured by the freezing-point method in benzene solution.

*Analyses.* Wt. of benzene, 16.22 g. Subs., 0.0812, 0.1984, 0.3367: depression, 0.129°, 0.327°, 0.539°. Mol. wt., calc.: 198. Found: 198.6, 187.5, 192.5; mean, 193.

Measurements of the density, the surface tension and the index of refraction were also made. These constants will be given together with the constants of the hydrocarbon prepared from tetrapropyl-glycol.

#### Preparation of Tetrapropyl-ethane from Tetrapropyl-glycol.

Three g. of tetrapropyl-glycol was reduced to the parent hydrocarbon by being heated at 180° in a sealed tube with 15 cc. of conc. hydriodic acid for 10 hours. The

<sup>5</sup> Kurtz, Ref. 3.

<sup>6</sup> Kurtz, Ref. 3, did not obtain the iodide in pure condition. He reported only 47.72% of iodine in his product.

reaction mixture of 6 combined lots was treated with sodium hydroxide and the remaining oil taken up with ether. The ether solution was washed with water and dried. After removal of the ether the main fraction distilled at 210–230°. The formation of free iodine and hydriodic acid showed that the product still contained some iodide. Another treatment with hydriodic acid removed all but traces of iodine. This last small amount was removed with zinc dust, acetic acid and alcohol.<sup>7</sup> The product thus obtained was halogen-free but with iodine it gave a brown color indicating the presence of an oxygen-containing compound. For the removal of this the oil was shaken with pure conc. sulfuric acid, separated and distilled over sodium. There was then obtained about 7 cc. of pure hydrocarbon which boiled at 220°. It gave a pink color with iodine and did not decolorize a very dilute solution of potassium permanganate. At a pressure of about 12 mm. of mercury it boiled at 107°. The hydrocarbon is a very thin liquid, which on cooling with solid carbon dioxide and ether became quite viscous but did not crystallize.

*Analyses.* Subs., 0.1187, 0.1502: CO<sub>2</sub>, 0.3690, 0.4680; H<sub>2</sub>O, 0.1610, 0.2045. Calc. for C<sub>14</sub>H<sub>30</sub>: C, 84.75; H, 15.25. Found: C, 84.79, 84.98; H, 15.18, 15.24.

The molecular weight was measured by the freezing-point method in benzene solution.

*Analyses.* Wt. of benzene, 16.27 g. Subs., 0.0944, 0.2137, 0.3919: depression, 0.149°, 0.333°, 0.617°. Mol. wt., calc.: 198. Found: 194, 197, 195; mean, 195.

The physical constants were measured under the same conditions under which they had been measured for the hydrocarbon prepared by the Wurtz reaction. The following table shows the identity of both hydrocarbons. The slight differences may be accounted for by traces of impurities that might be produced in either process. We assume that the hydrocarbon produced by the Wurtz reaction is the purer.

	Prepared by the	
	Wurtz Reaction.	Reduction of Pinacone.
B. p. at atm. pressure.....	220°	220°
B. p. at 12 mm.....	105–106°	107°
Density, 25°.....	0.7785	0.7749
Surface tension (measured with a Traube stalagmometer).....	25.64	25.31 dynes/cm.
Index of refraction (Abbe refractometer) at 25°.....	1.4322	1.4335
Consistency at room temperature....	very liquid	very liquid
Consistency at –80°.....	very viscous	very viscous.

### Summary.

Sym. tetrapropyl-ethane has been prepared by two synthetic methods and its physical properties measured. These data will be of value in further work on the reduction products of dimethyl-pyrone.

CHICAGO, ILLINOIS.

<sup>7</sup> Wislicenius, *Ann.*, 219, 312 (1883).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE THREE AMINO-TRIPHENYLAMINES.

BY JEAN PICCARD AND RAY Q. BREWSTER.<sup>1</sup>

Received August 9, 1921.

The three mononitro-triphenylamines are known. The *para* compound has been prepared by Richard Herz,<sup>2</sup> while the *o*- and the *m*-nitro-triphenyl amines were obtained by Piccard and Larsen.<sup>3</sup> Up to the present only the *para* compound has been reduced to the corresponding amino derivative.<sup>4</sup> Believing that the description of a nitro compound was not complete without the description of the corresponding amine and its acetyl derivative, the reduction of the nitro-triphenylamines newly prepared by Piccard and Larsen was undertaken. The reduction was carried out by Gambarjan's method with zinc dust in a solution of acetic acid and alcohol but the nitro compound was added very gradually to the reducing agent. In this way one avoids having simultaneously the nitro compound and an amino compound in the same solution. These two compounds are often able to react with the formation of disagreeable by-products.

### Experimental Part.

***m*-Amino-triphenylamine Hydrochloride.**—A solution of 1.9 g. of *m*-nitro-triphenylamine in 20 cc. of glacial acetic acid was added during the course of 10 to 15 minutes to a mixture of 8 g. of zinc dust, 6 cc. of absolute alcohol and 6 cc. of glacial acetic acid. Heat was evolved at each addition and the red color of the nitro compound faded rapidly. The liquid was filtered from the excess of zinc at the pump and washed with hot glacial acetic acid. Care was taken to draw as little air as possible through the zinc. The filtrate was made alkaline with a dilute solution of sodium hydroxide, and the precipitated base was removed by filtration, dissolved in ether and dried. Saturation of the ether solution with dry hydrogen chloride precipitated the hydrochloride of the *m*-amino-triphenylamine; yield, 1.9 g. This was dissolved in 400 cc. of hot water to which 15 cc. of conc. hydrochloric acid had been added. The solution was then decolorized with charcoal and cooled in a freezing mixture. About 1 g. of the hydrochloride crystallized in glistening colorless plates. An additional quantity (0.5 g.) could be precipitated out of the mother liquor by hydrogen chloride.

**Analyses.** Subs., 0.1374: 4.70 cc. of 0.1 *N* NaOH (methyl orange). Subs. 0.2287: AgCl, 0.1081.

<sup>1</sup> The material presented here is used by Ray Q. Brewster in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago (1919).

<sup>2</sup> Herz, *Ber.*, 23, 2537 (1890).

<sup>3</sup> Piccard and Larsen, *THIS JOURNAL*, 39, 2006 (1917).

<sup>4</sup> Herz, Ref. 2, was the first to prepare *p*-amino-triphenylamine although he published only a rough analysis of the hydrochloride and the acetyl derivative. Haussermann, *Ber.*, 39, 2763 (1906), isolated the base itself in a pure and stable form and published a good nitrogen determination. This work must have been overlooked by Gambarjan, *ibid.*, 41, 3507 (1908), who published a new description and analysis.

Calc. for  $C_{18}H_{17}N_2Cl$ : Cl, 11.96. Found: 12.12, 11.69.

The hydrochloride is very slightly soluble in water.

*m*-Amino-triphenylamine.—The *m*-amino-triphenylamine was precipitated from the aqueous solution of its hydrochloride by the addition of ammonium hydroxide. The base was dissolved in 95% ethyl alcohol, boiled with charcoal, filtered and allowed to crystallize. The substance was thus obtained in nearly colorless form, m. p.  $116^\circ$ . It is readily soluble in alcohol, ether and benzene.

*Analyses.* Subs., 0.1800, 0.1837: dry  $N_2$ , 17.0 cc. ( $15^\circ$  and 739 mm.), 17.6 cc. ( $19^\circ$  and 743 mm.). Calc. for  $C_{18}H_{15}N_2$ : N, 10.77. Found: 10.88, 10.94.

*m*-Acetyl-amino-triphenylamine.—One g. of the *m*-amino-triphenylamine was boiled for 15 minutes with 10 cc. of acetyl chloride. Water was added and the precipitated acetyl derivative recrystallized from alcohol, m. p.  $167^\circ$ .

*Analyses.* Subs., 0.1323:  $CO_2$ , 0.3865;  $H_2O$ , 0.0698. Calc. for  $C_{20}H_{15}ON_2$ : C, 79.49; H, 5.96. Found: C, 79.68, H, 5.94.

*o*-Amino-triphenylamine.—The *o*-nitro-triphenylamine was reduced in the manner just described for the *meta* compound. The crude yield was practically the calculated quantity. After recrystallization from alcohol the base was obtained in thin plates which had only a slight pink tint, and melted at  $145^\circ$ . It is readily soluble in alcohol and benzene but only fairly soluble in ether or ligroin.

*Analysis.* Subs., 0.1878: dry  $N_2$ , 17.7 cc. ( $16^\circ$  and 740 mm.). Calc. for  $C_{18}H_{15}N_2$ : N, 10.77. Found: 10.84.

*o*-Acetyl-amino-triphenylamine.—This compound was prepared in the same manner as the corresponding *meta* derivative. It is quite readily soluble in ether, alcohol and benzene, but only fairly soluble in ligroin; m. p.  $130^\circ$ .

*Analyses.* Subs., 0.1340:  $CO_2$ , 0.3905;  $H_2O$ , 0.0725. Calc. for  $C_{20}H_{15}ON_2$ : C, 79.49; H, 5.96. Found: C, 79.37; H, 6.10.

### Reduction of Nitro-triphenylamines in Concentrated Sulfuric Acid Solution.

L. Gattermann<sup>5</sup> has obtained *p*-aminophenol by the electrolytic reduction of nitrobenzene in conc. sulfuric acid solution. The same author has applied this method for the reduction of many other nitro compounds. Piccard and Larsen used it for the reduction of *m*-nitro-diphenylamine. It is surprising, that *m*-nitro-triphenylamine and *o*-nitro-triphenylamine cannot be reduced by this method to the corresponding *p*-oxy derivatives. We obtained in both cases only high molecular compounds with a lower nitrogen content than the one calculated for the diphenylamino-*p*-aminophenols.

### Summary.

1. The *o*- and *m*-amino triphenylamines have been prepared and characterized. Since the *para* derivative is already known the series is now complete.

2. Attempts to reduce the nitro-triphenylamines to their corresponding amino phenols met with no success.

CHICAGO, ILLINOIS.

<sup>5</sup> Gattermann, *Ber.*, 26, 1846 (1893).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 377.]

## UNIFORMITY IN INVERTASE ACTION.

BY J. M. NELSON AND DAVID I. HITCHCOCK.

Received August 13, 1921.

## I. Introduction.

The study of the nature of enzymes has developed chiefly along two distinct lines. So far all attempts to isolate an enzyme as a pure substance of definite chemical composition have been without satisfactory results. Accordingly considerable work has been done to gain an insight into the nature of the enzyme itself by studying the velocity of the reaction which is catalyzed by the enzyme. The object in all these researches on the chemical kinetics of enzyme action has been to find some general law governing the rate of the reaction, and by means of this to make deductions concerning the mechanism of the action and the nature of the enzyme.

In all such work the tacit assumption has been made that any two preparations of the same enzyme, if the same amount of active enzyme is present, and other conditions are the same, will catalyze the reaction at identical rates at corresponding points throughout. In other words, if the course of the reaction were plotted, the two curves should be superimposable. While this assumption has not been definitely stated in the past, it is a necessary implication of the attempt to find a general law for the rate of the catalyzed reaction. Accordingly it seemed desirable, before going further in the attempt to obtain a general law for the hydrolysis of cane sugar by the catalytic action of invertase, to find out by direct experiment whether several different enzyme preparations would really give the same quantitative course to the reaction.

## II. Differences in Invertase Action.

In order to make this comparison, it was necessary to have all the conditions alike except for the use of different invertase preparations. The conditions adopted were a temperature of 25°, an initial sucrose concentration of 10 g. per 100 cc., and a hydrogen-ion concentration of  $10^{-4.4}$  to  $10^{-4.5}$  secured by 0.01 *M* buffer solution of acetic acid and sodium acetate. The amounts of invertase were so adjusted in each experiment that the reaction started off at the same rate. This was accomplished by a few preliminary experiments, making use of the fact noted by Nelson and Vosburgh,<sup>1</sup> that the velocity of inversion is directly proportional to the concentration of the enzyme. The extent of inversion was determined by the polariscopic method. That this method is justifiable has been established by Vosburgh<sup>2</sup>.

<sup>1</sup> Nelson and Vosburgh, *THIS JOURNAL*, 39, 790 (1917).

<sup>2</sup> Vosburgh, *ibid.*, 43, 219 (1921).



Table I contains the results of 10 experiments with 4 different invertase preparations. These preparations were all obtained from yeast by modifications of the method of Nelson and Born. No differences in the method of preparation are known which might account for the abnormality of No. 3. Further description of the method of preparation will be found under the heading "Experimental Details."

TABLE I.  
DIFFERENCES IN INVERTASE ACTION.

Temp., 25°. Conc. of sucrose, 10 g. per 100 cc. Conc. H<sup>+</sup>, 10<sup>-4.4</sup> to 10<sup>-4.5</sup> moles per liter.

A. Normal Invertase.								
Expt.	B1.	B2.	B5.	B6.	B9.	B10.	Mean.	
Invertase Preparation No.	8.	8.	2.	2.	1.	1.		
Cc. of Invertase per 100 cc.	1.530.	1.530.	7.141.	7.141.	6.080.	6.080.		
Initial Rotation, degrees.	13.05.	13.04.	13.17. <sup>a</sup>	13.18. <sup>a</sup>	13.05.	13.04		
Time t. Min.	Change in rotation, degrees.						Inverted p %.	
5	0.54	0.54	0.53	0.54	0.52	0.51	0.53	3.15
10	1.07	1.07	1.07	1.07	1.06	1.06	1.07	6.35
15	1.58	1.59	1.58	1.59	1.58	1.57	1.58	9.38
22	2.33	2.34	2.32	2.31	2.31	2.31	2.32	13.77
30	3.12	3.14	3.12	3.12	3.12	3.12	3.12	18.52
60	5.97	5.98	5.97	5.96	5.98	5.97	5.97	35.43
90	8.47	8.48	8.46	8.44	8.50	8.49	8.47	50.27
120	10.57	10.59	10.55	10.54	10.58	10.59	10.57	62.73
180	13.52	13.53	13.53	13.50	13.55	13.53	13.53	80.30
300	15.93	15.93	15.91	15.93	15.93	15.91	15.92	94.48
2 to 4 days	16.87	16.86	16.85	16.87	16.85	16.85	16.86	.....
B. Abnormal Invertase.								
Expt.	B12.	B13.	B14.	B15.	Mean.			
Invertase Preparation No.	3.	3.	3.	3.				
Cc. of Invertase per 100 cc.	1.905.	1.905.	1.905.	1.905.				
Initial Rotation, degrees.	13.05.	13.05.	13.05.	13.05.				
Time. t. Min.	Change in rotation, degrees.				Inverted p %.			
15	0.55	0.54	0.54	0.54	0.54	0.54	3.20	
10	1.07	1.08	1.07	1.07	1.07	1.07	6.35	
15	1.59	1.59	1.59	1.57	1.59	1.59	9.44	
22	2.30	2.31	2.29	2.30	2.30	2.30	13.65	
30	3.13	3.11	3.10	3.08	3.11	3.11	18.46	
60	5.92	5.87	5.88	5.88	5.89	5.89	34.96	
90	8.33	8.30	8.32	8.31	8.32	8.32	49.38	
120	10.39	10.34	10.36	10.35	10.36	10.36	61.48	
180	13.27	13.26	13.30	13.28	13.28	13.28	78.81	
300	15.77	15.73	15.78	15.81	15.77	15.77	93.58	
2 to 4 days	16.85	16.85	16.85	16.85	16.85	16.85	....	

<sup>a</sup> The high values of these figures are due to the fact that invertase No. 2 itself had an unusually high rotation.

It will be noticed that the results indicate that in 6 experiments with 3 different invertase preparations the invertase is acting alike throughout

the course of the reaction. The results of the last 4 experiments, on the other hand, while agreeing among themselves, do not agree well with the other results beyond about the first 20% of the inversion. This indicates that invertase preparation No. 3 is in some way different from the other preparations, since the latter part of the reaction is noticeably slower. These results therefore show that not all preparations of invertase have, under a given set of conditions, the same degree of activity. It was thought at first that this retardation might be due to spontaneous destruction of the enzyme. That this was not the case is shown by the results of experiment B15, for in this case the invertase was kept in the thermostat for 5 hours before the start of the reaction. It has been shown by O'Sullivan and Tompson<sup>3</sup> that invertase suffers spontaneous destruction less rapidly in the presence of sucrose than in its absence. Since the results of Expt. B15 indicate no loss in activity of the invertase in 5 hours without the presence of sucrose, it is evident that the difference in the action of invertase preparation No. 3 cannot be due to spontaneous destruction of the enzyme. Table I proves, therefore, that while there seems to be a normal course for invertase action, there are also exceptions or abnormal invertase preparations.

### III. Discussion of Equations for Invertase Action.

If a general equation for normal invertase action were available, it would be comparatively easy to ascertain from experimental data whether any given preparation were normal or abnormal. Nelson and Vosburgh<sup>1</sup> and others have shown that the rate of hydrolysis of cane sugar by invertase is not proportional to the concentration of the substrate, or, in other words, the reaction does not obey the unimolecular law,

$$\frac{1}{t} \log \frac{a}{a-x} \quad (1)$$

where  $k$  is the velocity coefficient,  $t$  time in minutes,  $a$  the initial cane sugar concentration and  $x$  the amount hydrolyzed.

Henri<sup>4</sup> proposed an empirical equation containing only one constant.

$$k = \frac{1}{t} \log \frac{a+x}{a-x}. \quad (2)$$

When this equation was applied to the results with normal invertase given in Table IA, decreasing values for the constant were obtained.

Equations of the form

$$t = k_1 \log \frac{a}{a-x} + k_2 x. \quad (3)$$

<sup>3</sup> O'Sullivan and Tompson, *J. Chem. Soc.*, 57, 834 (1890).

<sup>4</sup> Henri, "Lois générales de l'action des diastases," Hermann, Paris, 1903, p. 59.

were deduced by Henri<sup>5</sup> and Bodenstein,<sup>6</sup> by Barendrecht,<sup>7</sup> Michaelis and Menten,<sup>8</sup> and Van Slyke and Cullen.<sup>9</sup> On applying the method of least squares to the present results (Table IA) to determine the constants for an equation of this type, it was found that such an equation would not hold satisfactorily for the whole course of the reaction. However, by using the values obtained for the first half of the hydrolysis only, the following equation, obtained by least squares, was found to hold for the first 50% of the hydrolysis.

$$t = 135.2 \log \frac{100}{100-p} + 0.9724 p. \quad (4)$$

Here  $t$  is the number of minutes required for  $p$  per cent. of the sucrose to be inverted. When  $p$  is expressed in the notation of Equation 1 it is equal to  $100 x/a$ . The accuracy with which the equation fits the results may be seen from the following figures.

$p$ .	$t$ (calc.).	$t$ (obs.).	$p$ .	$t$ (calc.).	$t$ (obs.).
3.15	4.94	5	18.52	30.0	30
6.35	10.0	10	35.43	60.1	60
9.37	14.9	15	50.27	89.9	90
13.77	22.1	22			

By considering the hydrolysis of sucrose as a reversible reaction, uni-molecular in one direction and bimolecular in the other, Visser<sup>10</sup> deduced an equation which, in the symbols previously used, takes the form

$$\frac{dx}{dt} = k_1(a-x) - k_2x^2. \quad (5)$$

On applying this to his experiments he obtained increasing values for a quantity which should theoretically have been constant. In order to correct for this increase he introduced a factor  $I$  to which for some reason he attributed a chemical significance, and called it "the intensity of the enzyme," giving the equation:

$$\frac{dx}{dt} = [k_1(a-x) - k_2x^2]I. \quad (6)$$

The values of  $I$  he obtained from the increasing values of the constant obtained from Equation 5, and he found they could be expressed by the empirical formula

$$I = \frac{k_3}{7a^2 - 4ax + x^2}. \quad (7)$$

By substituting this expression in Equation 6 and integrating he obtained

<sup>5</sup> *Op. cit.*, p. 79.

<sup>6</sup> Bodenstein, *ibid.*, p. 92.

<sup>7</sup> Barendrecht, *Z. physik. Chem.*, 49, 456 (1904).

<sup>8</sup> Michaelis and Menten, *Biochem. Z.*, 49, 333 (1913).

<sup>9</sup> Van Slyke and Cullen, *J. Biol. Chem.*, 19, 141 (1914).

<sup>10</sup> Visser, *Z. physik. Chem.*, 52, 257 (1905).

a complicated equation which gave constants satisfactory to about  $\pm 10\%$ . Since Hudson<sup>11</sup> has shown Visser's theory of reversibility to be unsound, no attempt was made to apply this equation to the present results.

Visser also proposed a simpler equation for invertase action, obtained by neglecting the reverse reaction, but putting the same factor  $I$  into the unimolecular equation.

$$\frac{dx}{dt} = k(a-x)I = k(a-x) \frac{d_2}{7a^2 - 4ax + x^2} \quad (8)$$

This on integration becomes

$$2k_1 k_2 t = 8a^2 \ln \frac{a}{a-x} + x(6a-x) \quad (9)$$

Visser's application of this equation to his own experiments gave "constants" which showed an extreme variation of 30% (0.00108 to 0.00139) and an application of the same equation to the experiments of Table IA likewise gave increasing values for the constant.

An equation of similar form,

$$t = k_1 \log \frac{a}{a-x} + k_2 x + k_3 x^2, \quad (10)$$

was obtained from the data of Table IA by the method of least squares, but did not fit the experimental data well enough to be of any use in the present work.

In order to get satisfactory agreement with the experimental data, it was found necessary to use an equation containing four constants. The following equation was obtained by applying the method of least squares to the mean results of the 6 experiments in Table IA.

$$t = 222.9 \log \frac{100}{100-p} + 0.5890p - 0.001975p^2 - 0.00002034p^3. \quad (11)$$

The applicability of this equation may be seen from the following figures.

TABLE II.  
APPLICATION OF EMPIRICAL EQUATION.

Inversion. p %	Time. t(calc.). Min.	Time. t(obs.). Min.	$n \times 10^4$ <sup>a</sup>
3.15	4.96	5	443
6.35	10.1	10	449
9.38	14.9	15	445
13.77	22.1	22	449
18.52	30.1	30	447
35.43	60.0	60	446
50.27	89.8	90	445
62.73	119.6	120	445
80.30	180.6	180	448
94.48	299.9	300	447

Mean, 446

A. d., 0.36%.

<sup>a</sup> Meaning of  $n$  explained below.

<sup>11</sup> Hudson, THIS JOURNAL, 36, 1571 (1914).

#### IV. An Equation for Experiments with Different Amounts of Invertase.

Nelson and Vosburgh<sup>1</sup> showed that, in their experiments in which the initial sucrose concentration was constant, the time required for a given percentage of sucrose to be inverted was inversely proportional to the amount of invertase used. In other words, letting  $t$  represent the time for 80% inversion, and  $y$  the invertase concentration, in experiments in which only the invertase concentration was varied they found the product  $ty$  to be constant. In another series of experiments with a different invertase preparation they called  $t$  the time for 40% inversion, and here again  $ty$  was constant. They did not, however, compare the times for different degrees of inversion in any one experiment, say  $t$  for 40% and  $t$  for 80% inversion, because they did not know the law governing the relationship between the time and the percentage of inversion, or, mathematically, the form of the function,  $t=f(p)$ .

It is obvious that one may plot the values for the amounts hydrolyzed in various times against the times, obtaining curves for the hydrolyses which are graphical representations of the function,  $t=f(p)$ . This was done by Michaelis and Davidsohn<sup>12</sup> in such a way as to compare the form of the function in three experiments with invertase concentrations in the ratio 2:1:0.4. They plotted the product of the enzyme concentration and the time,  $ty$ , against the change in rotation, which is proportional to the percentage inverted,  $p$ . They claimed that the points all fell on a smooth curve, and that therefore the form of the hydrolysis curve was independent of the amount of enzyme. However, only 3 experiments were given of which one was represented by only 2 points. Moreover, their whole curve did not appear to extend much beyond the first half of the inversion, and in addition several of their points did not fall on the curve, even on the small scale used in their printed article. Because of these deficiencies, and because the shape of the curve is a fundamental point in the present investigation, it seemed best to amplify their data by the use of the more extensive experiments of Nelson and Vosburgh.

Accordingly the results of the latter were plotted in a similar way on a large scale. The curves were brought together at one point by using a different time scale for each experiment. When the remainder of each curve was plotted on this new scale, it was found that the curves for experiments with the same initial sucrose concentration did superimpose, falling on a single smooth curve. Thus the conclusion drawn by Michaelis and Davidsohn was more firmly established by the results of Expts. 6, 7, 8, 9, 10, 22 and 23 of Nelson and Vosburgh, each experiment including at least 6 samples and extending over 95% or more of the inversion. This means that the function,  $t=f(p)$ , representing a single experiment, can be generalized as  $nt=F(p)$  for experiments with varying amounts of invertase.

<sup>12</sup> Michaelis and Davidsohn, *Biochem. Z.*, 35, 386 (1911).

Here  $n$  is a constant in any one experiment, but varies in different experiments, being proportional to the amount of effective invertase. Moreover the form of the function  $nt = F(p)$  is, within the limits of these experiments, independent of the amount of invertase or of the rate of the hydrolysis.

A more exact verification of this relationship was obtained by the use of Equation 11, which gives a definite form to the function,  $t = f(p)$ , for one particular invertase concentration. In order to make this equation generally applicable to experiments with other invertase concentrations, the coefficient of the logarithmic term was placed equal to  $1/n$  and factored out, giving

$$t = \frac{1}{n} \left[ \log \frac{100}{100-p} + 0.002642p - 0.000008860p^2 - 0.0000001034p^3 \right]. \quad (12)$$

If it is generally true that the times for any given percentage of inversion are inversely proportional to the amounts of invertase used, then Equation 12 gives a definite form to the function,  $t = f(p)$ , for any invertase concentration. Whether or not this is the case can be tested by substituting in Equation 12 the experimental values for  $p$  and  $t$ , and calculating the values of  $n$ . If the latter are constant, the equation applies and the general law holds, and the values of  $n$  should be directly proportional to the amounts of active invertase present.

To recapitulate, we have, if this is true, first an empirical relation between time and percentage inverted which holds for experiments in which different amounts of invertase are used; and, second, we have in the value of  $n$  a relative measure of the amount of the effective invertase.

In order to decide whether or not Equation 12 applies to a given experiment, it is necessary to decide whether or not the values of  $n$  are constant. The values of  $n$  for the experiments of Table IA, from which the equation was derived, are given in the last column of Table II. The average deviation from the mean, 0.36%, is an indication of the extent to which the equation fits these original experiments. To determine about what magnitude of deviation from the mean might be due to experimental error in applying the equation to other experiments, the following calculations were made.

From the agreement of duplicate experiments in Table I and subsequent experiments, the average error in determining any change in rotation was estimated as  $0.02^\circ$ . To determine what error in  $n$  could be caused by such an error, the value  $0.02^\circ$  was added to all the changes in rotation of Table IA, and the values of  $n$  recalculated, with the results shown in Table III.

Evidently the form of the relationship is such that errors are magnified in the values of  $n$  calculated from the data on the early part of the hydrolysis. Since in all the experiments of the present work except those of Table I the first sample was taken at about 10% inversion, while the

TABLE III.

Effect of assumed error of  $0.02^\circ$ .

$p$ + error.	$t$ .	$10\%n$ (+ error).	$10\%n$ (true values).	Error in $10\%n$ .	Dev. from true mean.
3.26	5	458	443	15	12
6.47	10	457	449	8	11
9.50	15	450	445	5	4
13.89	22	453	449	4	7
18.64	30	450	447	3	4
35.55	60	448	446	2	2
50.39	90	446	445	1	0
62.85	120	446	445	1	0
80.42	180	450	448	2	4
94.60	300	450	447	3	4

Mean, 4.4 = 0.99%.

Mean, 4.8 = 1.08%.

other 7 samples were distributed about as before, it was decided that a fairer measure of the average error in  $n$  would be given by the mean of the last 8 of the above values. This gives an average deviation of 0.59% from the individual values of  $n$ , or of 0.70% from the mean value of  $n$  as the deviation caused by an error of  $0.02^\circ$  in the value of each change in rotation. Hence it may fairly be decided that any experiment giving an average deviation from the mean of 0.7% or less is fitted by the equation, and its curve has the same shape or the function,  $nt = F(p)$ , has the same form as in the case of the original experiments of Table IA.

Since the results of Nelson and Vosburgh were available, including experiments in which the concentration of invertase was varied, it was thought that these results might well be used as a test of the general applicability of Equation 12. Accordingly Table IV was prepared by using those of their experiments in which the initial sucrose concentration was 10 g. per 100 cc.

In the last three of these experiments the average deviation from the mean of the values of  $n$  is below the value 0.7%. As has been already pointed out, this deviation might be caused by experimental error, and accordingly the equation fits these three experiments satisfactorily. In Expts. 6, 8, and 9 the first sample was taken before the inversion was 10% complete. Now it has been already pointed out that in this part of the inversion a small experimental error may cause a large error in the value of  $n$ . Accordingly for these experiments the mean of the remaining values of  $n$  was calculated, omitting the first, and the average deviations were found to be 0.64%, 0.40%, and 0.10% for Expts. 6, 8 and 9, respectively. Therefore the equation really does fit 6 of the 7 experiments in Table IV, and it may be concluded with more certainty than before that the shape of the hydrolysis curve or the form of the function,  $nt = F(p)$ , is independ-

TABLE IV.

EFFECT OF VARYING AMOUNTS OF INVERTASE. (EXPERIMENTS OF NELSON AND VOSBURGH.)

Initial sucrose concentration, 10 g. per 100 cc. Hydrogen-ion concentration,  $3.2 \times 10^{-5}$  to  $2.1 \times 10^{-5}$  moles per liter. Temperature,  $37^{\circ}$ . Invertase preparation A used in Expts. 6 to 10, Preparation B in Expts. 22 and 23.

Expt.	Inv. per 100. Cc.	Time. $t$ , Min.	Amt. inverted, $p$ , %.	$n \times 10^4$ .	Expt.	Inv. per 100. Cc.	Time $t$ , Min.	Amt. inverted, $p$ , %.	$n \times 10^4$ .
6	6	14	8.32	422	7	5	22	11.08	360
		30	17.92	433			40	20.15	366
		70	39.85	437			90	43.21	372
		120	61.90	437			138	60.98	372
		185	80.59	439			215	80.30	375
		320	94.97	431			373	95.04	370
		Mean,	433				Mean,	369	
		Average dev.,	1.04%.				Average dev.,	1.14%.	
8	4	20	8.31	295	9	3	33	9.57	206
		45	18.69	301			70	20.49	213
		105	41.17	302			150	41.50	213
		175	62.11	301			250	62.44	212
		265	80.09	303			376	80.09	213
		450	94.85	305			660	95.28	213
		Mean,	301				Mean,	212	
		Average dev.,	0.73%.				Average dev.,	0.80%.	
10	2	50	10.01	143	22	1	30	10.91	259
		100	20.14	146			60	21.50	261
		221	42.09	147			122	41.21	260
		315	56.10	146			200	61.49	260
		345	60.04	146			305	79.65	260
		570	81.60	147			600	96.08	(248) <sup>a</sup>
		1365	98.06	(131) <sup>a</sup>			Mean,	260	
		Mean,	146				Average dev.,	0.17%.	
		Average dev.,	0.57%.						
23	2	14	10.34	526					
		28	20.49	533					
		60	41.81	538					
		100	62.62	533					
		156	81.70	537					
		280	95.70	(517) <sup>a</sup>					
		Mean,	533						
		Average dev.,	0.60%.						

<sup>a</sup> These values are for points beyond the limit of  $p$ , 95%, for which the equation was derived, and hence were not used in taking the mean.

ent of the invertase concentration, and that Equation 12 gives a definite form to this function,  $F(p)$ .

In view of the fact that the extreme variation in the invertase concentration in these experiments was from 6 cc. to 2 cc. or in the ratio 3:1, while the range covered by the rather unsatisfactory experiments of Michaelis and Davidsohn was 5:1, it seemed best to try the effect of a wider variation



in invertase concentration on the shape of the curve. The highest concentration used was selected so as to make the hydrolysis as rapid as possible without causing error in the timing of samples, and the lowest concentration was such that the first and last samples could just conveniently be taken on the same day. In view of the difficulty encountered in a previous investigation<sup>13</sup> in obtaining reproducible results with very dilute invertase solutions, it seemed unwise to attempt to study slower reactions than this. The results of the experiments with the extreme invertase concentrations used, in the ratio 12:1, are given in Table V.

TABLE V.

EXTREME CHANGES IN INVERTASE CONCENTRATION.								
Expts. B60 and B61.					Expt. B62.			
6 cc. of Invertase 8 per 100 cc.					0.5 cc. of Invertase 8 per 100 cc.			
Time, t, Min.	Rotation, B60, Degrees.	B61.	Amt. inverted, p, %.	$n \times 10^4$ .	Time, t, Min.	Rotation, degrees.	Amt. inverted, p, %.	$n \times 10^4$ .
0	13.09	13.09	.....	...	0	13.04	.....	...
5	11.11	11.11	11.75	168	60	11.11	11.45	136
10	9.24	9.25	22.85	167	120	9.28	22.31	136
15	7.50	7.51	33.18	166	180	7.58	32.40	135
21	5.57	5.58	44.63	166	252	5.68	43.68	135
28	3.59	3.59	56.38	165	336	3.76	55.07	134
37	1.49	1.49	68.84	166	444	1.70	67.30	133
52	-0.93	-0.94	83.26	168	624	-0.70	81.54	134
70	-2.43	-2.43	92.11	170	840	-2.26	90.80	134
1-7 days	-3.76	-3.76	Mean,	167	11 days	-3.81	Mean,	135
			Av. dev.,	0.75%			Av. dev.,	0.65%

The values of  $n$  are sufficiently constant so that the equation may be said to hold for these concentrations.

If the time for any given percentage of inversion is inversely proportional to the concentration of invertase, the value of  $n$  divided by the number of cubic centimeters of invertase used per 100 cc. of solution should be a constant for any given invertase preparation. For Expts. B1 and B2 (Table IA) this value is 0.00292; for Vosburgh and Nelson's Expt. 1B (Table VI), it is 0.00290; for B60 and B61, 0.00278; and for B62, 0.00270. These experiments were all made with Invertase 8. The difference between the former two and the latter two values is due to slow deterioration of the invertase, even when kept in the ice-box, for a period of 8 months had elapsed between the two sets of experiments. The smaller difference between the latter two values can hardly be so explained, as the experiments were run on successive days, but must be taken to mean that for this range of concentrations the effective activity of the invertase is not strictly proportional to the actual concentration used. However, since the equation applies equally well in both cases, it may be stated as a fact

<sup>13</sup> Nelson and Hitchcock, "The Activity of Adsorbed Invertase," *THIS JOURNAL*, 43, 1956 (1921).

that over this range of invertase concentrations (12:1) the form of the function,  $nt = F(p)$ , is the same and is expressed by Equation 12, while the value of  $n$  represents accurately the true activity of the invertase even better than its relative concentration.

### V. Effect of Temperature.

Since the experiments of Nelson and Vosburgh were carried out at 37° while the present experiments were run at 25°, it seemed that the effect of temperature differences in any two experiments might be constant for all stages of the reaction. Inasmuch as some experiments on the course of the hydrolysis at various temperatures had recently been made in this

TABLE VI.

EFFECT OF TEMPERATURE. (EXPERIMENTS OF VOSBURGH AND NELSON.)

Initial sucrose concentration, 10 g. per 100 cc. Hydrogen-ion concentration,  $4.4 \times 10^{-5}$  to  $4.0 \times 10^{-5}$  moles per liter. Invertase preparation No. 8, 1 cc. per 100 cc.

Expt.	Temp.	Time,	Amt.	$n \times 10^5$	Expt.	Temp.	Time,	Amt.	$n \times 10^5$
°C.		t, Min.	inverted, p, %.		°C.		t, Min.	inverted, p, %.	
11B	15	21	5.22	175	15B	20	16	5.04	222
		63	14.54	166			38	11.87	223
		110	24.39	163			65	19.82	222
		162	34.72	162			120	34.90	220
		250	50.45	161			155	43.68	219
		350	65.04	161			190	51.40	217
		441	75.07	161			254	63.92	216
		586	85.88	162			320	74.18	217
		Mean,	164				420	84.87	218
		Av. dev.,	2.07%.				Mean,	219	
							Av. dev.,	0.96%.	
1B	25	15	6.17	290	5B	30	9	4.93	381
		36	14.60	292			29	15.07	374
		63	24.80	289			50	25.22	371
		105	39.70	290			71	35.05	373
		165	57.39	287			107	49.79	370
		235	73.24	289			153	65.34	370
		360	88.84	290			190	75.07	373
		Mean,	290				246	84.93	374
		Av. dev.,	0.34%.				Mean,	373	
							Av. dev.,	0.60%.	
7B	35	8	5.46	482					
		24	15.76	473					
		42	26.59	467					
		60	36.91	467					
		90	52.11	465					
		120	64.63	464					
		155	76.02	467					
		195	84.93	471					
		Mean,	469						
		Av. dev.,	0.91%.						

laboratory by Vosburgh and Nelson,<sup>14</sup> it seemed inadvisable to repeat this work. Accordingly the effect of temperature on the shape of the hydrolysis curve was tested by applying Equation 12 to these experiments, with the results shown in Table VI.

In all of these experiments the first sample was taken at a point considerably below 10% inversion. Therefore, in order to compare the average deviation with that which might be due to experimental error, the values obtained from the first sample should be omitted in taking the mean. If this is done the values for the average deviation are as follows: Expt. 11B, 0.68%; 15B, 0.91%; 1B, 0.34%; 5B, 0.43%; and 7B, 0.56%. All of these except that for Expt. 15B are less than 0.7%, and accordingly Equation 12 fits these experiments fairly well. This establishes for the first time the fact that temperature differences, at least between 15° and 35°, have no effect on the shape of the hydrolysis curve or the form of the function,  $nt = F(p)$ . In other words, an increase in the temperature has the same quantitative effect as an increase in the amount of the invertase used.

#### VI. Effect of Hydrogen-ion Concentration.

In his classical study of the effect of hydrogen-ion concentration on invertase action, Sørensen<sup>15</sup> found that the velocity coefficient  $k$  calculated according to the unimolecular law in the form

$$k = \frac{1}{t_2 - t_1} \ln \frac{a - x_1}{a - x_2}$$

increased considerably as the reaction progressed in nearly neutral solutions ( $C_{H^+} = 10^{-6}$  to  $10^{-7}$ ), increased less around the optimum ( $C_{H^+} = 10^{-4}$  to  $10^{-5}$ ), remained constant in slightly more acid solutions ( $C_{H^+} = 1.2 \times 10^{-4}$ ), and decreased in still more acid solutions ( $C_{H^+} = 2.1 \times 10^{-4}$ ). This means that the shape of the hydrolysis curve or the form of the function  $nt = F(p)$  was not the same, in his experiments, for different hydrogen-ion concentrations. Michaelis and Davidsohn<sup>12</sup> have pointed out that this variation may be explained in part by destruction of the invertase in the more acid solutions at the rather high temperature, 52°, at which Sørensen carried on his experiments. By using a lower temperature, 22.3°, they obtained values of  $k$  calculated from the equation

$$k = \frac{1}{t} \log \frac{a}{a - x}$$

which increased in experiments at hydrogen-ion concentrations less than  $3.0 \times 10^{-3}$ , where they remained constant. Nelson and Vosburgh,<sup>1</sup> on the other hand, found that at 37° the values of  $k$  increased in experiments

<sup>14</sup> Vosburgh and Nelson, "The Temperature Coefficient of Invertase Action," (to be published later).

<sup>15</sup> Sørensen, *Biochem. Z.*, 21, 131-304 (1909); also *Compt. rend. Lab. Carlsberg*, 8, 1 (1909).

at the optimum hydrogen-ion concentration,  $3.2 \times 10^{-5}$ , but increased more slowly or remained constant at  $3.2 \times 10^{-6}$ . They noticed, however, that there were some changes in the hydrogen-ion concentration during the latter half of the inversion at about  $3.2 \times 10^{-6}$ .

The equation of the present work will not fit experiments in which the values of the unimolecular " $k$ " are constant or decrease, because it was derived for experiments for which the unimolecular " $k$ " increased. In order to test the effect of hydrogen-ion concentration on the shape of the curve the equation was applied to some recent experiments of Vosburgh and Nelson (to be published later) in which the hydrogen-ion concentration was held constant at  $10^{-6}$  moles per liter by means of citrate buffers and the improved procedure recommended by Vosburgh<sup>18</sup> was used. These results are given in Table VII.

TABLE VII.

EFFECT OF A DIFFERENT HYDROGEN-ION CONCENTRATION. (EXPERIMENTS OF VOSBURGH AND NELSON.)

Initial sucrose concentration, 10 g. per 100 cc. Hydrogen-ion concentration,  $1.10 \times 10^{-6}$  to  $1.13 \times 10^{-6}$  moles per liter. Invertase preparation No. 8, 1 cc. per 100 cc.

Expt.	Temp. C.	Time, Min.	Amt. inverted, p, %.	$n \times 10^4$ .	Expt.	Temp. C.	Time, Min.	Amt. inverted, p, %.	$n \times 10^4$ .
13B	15	23	4.99	153	2B	25	30	11.10	264
		75	15.43	148			55	19.76	261
		126	25.34	148			80	28.13	261
		178	35.67	148			101	34.84	260
		282	51.57	147			138	45.58	258
		390	65.46	146			217	64.87	258
		490	75.43	146			350	84.69	261
		642	85.52	146				Mean,	260
			Mean,	148				Av. dev.,	0.62%.
			Av. dev.,	1.01%.					
9B	35	10	5.88	415					
		26	15.01	415					
		44	24.75	413					
		64	35.10	414					
		98	50.56	412					
		135	64.45	411					
		171	74.96	413					
		225	85.52	416					
			Mean,	414					
			Av. dev.,	0.34%.					

Except for the first value in Expt. 13B, the deviation of which may be due to a slight experimental error, as has been already pointed out, the constancy of  $n$  is very satisfactory. This means that at a hydrogen-ion concentration of  $10^{-6}$  moles per liter the curve has the same shape or the

<sup>18</sup> Vosburgh, "Some Errors in the Study of Invertase Action," THIS JOURNAL, 43, 1693 (1921).

function  $nt=F(p)$  has the same form as at the optimum hydrogen-ion concentration. The differences found by Nelson and Vosburgh<sup>1</sup> at  $C_{H^+} + 3.2 \times 10^{-6}$  must be ascribed to changes in the hydrogen-ion concentration or in the amount of active invertase due to the use of hydrochloric acid without buffer. The nature of the buffer, however, does not seem to affect the shape of the curve, for the experiments of this present work were made with a 0.01 *M* buffer mixture of acetic acid and sodium acetate, while the experiments of Vosburgh and Nelson (Tables VI and VII) were made with a similar concentration of sodium citrate. Very recently the range for which the equation has been extended to  $C_{H^+} + 3.2 \times 10^{-7}$  by some experiments of Bloomfield (not yet published). These results mean that within the limits given changes in hydrogen-ion concentration affect the activity of the invertase in just the same way as changes in temperature or in the amount of invertase used; either there is actually a change in the amount of the active substance present throughout the experiment or else the activity of the amount present is uniformly reduced or increased by the change and remains constant throughout the experiment.

### VII. A Criterion of Normal Invertase Action.

Above, in Part II of this paper, experiments were given which showed that not all invertase preparations impart the same shape to the hydrolysis curve. Equation 12 was made to fit the experiments in Table IA, made with invertase preparations which were classified as normal. Accordingly it seemed probable that it would not fit the experiments in Table IB, and hence might be used as a means of distinguishing between normal and

TABLE VIII.

APPLICATION OF THE EQUATION AS A CRITERION OF NORMAL INVERTASE ACTION.

Expts. B12-15.				Expts. B17 and B18.			
1.905 cc. of Invertase 3 per 100 cc.				10.45 cc. of Invertase 6 per 100 cc.			
Time <i>t</i> , Min.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .	Time, <i>t</i> , Min.	Rotation, B17. Degrees.	B18.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .
0	0	...	0	13.15	13.15	0	...
5	3.20	450	15	11.47	11.46	10.03	476
10	6.35	449	30	9.88	9.88	19.41	470
15	9.44	448	50	7.90	7.90	31.16	466
22	13.65	445	70	6.10	6.10	41.84	461
30	18.46	446	90	4.52	4.49	51.34	457
60	34.96	440	115	....	2.75	61.72	454
90	49.38	436	140	1.35	1.32	70.15	451
120	61.48	433	180	-0.36	-0.40	80.30	448
180	78.81	431	240	-1.95	-1.96	89.67	449
300	93.59	426	300	-2.74	-2.74	94.30	443
	Mean, 440	2 to 7 days		-3.71	-3.71	Mean,	457
	Av. dev., 1.4%.					Av. dev., 1.9%.	

abnormal invertase preparations. Equation 12, therefore, was applied to the results of Table IB, and also to experiments with two other invertase preparations, Nos. 6 and 7, with the results shown in Table VIII.

Expts. B20 and B21.				
3.60 cc. of Invertase 7 per 100 cc.				
Time, M.	B20.	Rotation, Degrees.	B21.	Amt. inverted, p. %.
			13.08	0
			11.47	453
	.89		9.91	456
	7.94		7.96	454
	6.17		6.16	451
	4.53		4.54	450
117	2.64		2.66	448
140	1.29		1.33	448
180	-0.49		-0.43	449
240	-2.06		-2.06	452
300	-2.85		-2.81	446
2 to 7 days	-3.78		-3.78	Mean, 450
				Av. dev., 0.56%.

It will be noticed in Expts. B12-15, Table VIII, that for those points where the data of Table IB coincided with those of Table IA, or up to 20% of the inversion, the values of  $n$  are fairly constant, even for abnormal invertase. The abnormality, however, shows up later in the decreasing values of  $n$ , and is indicated by the larger values of the average deviation of a single value of  $n$  from the mean, which is well above 0.7% for the experiments with Invertase 3. Expts. B17 and B18 indicate that Invertase 6 is also an abnormal invertase preparation, since the values of  $n$  decrease and the average deviation is well above 0.7%. Invertase 7, on the other hand, is a normal invertase preparation, as is shown by Expts. B20 and B21, since the values of  $n$  exhibit satisfactory constancy. These experiments indicate that Equation 12 may be used as a criterion of normal invertase action. In order to decide whether invertase preparations are normal or abnormal, then, it is no longer necessary to use them at initially equivalent effective concentrations, but the experiments may be made with any concentration, at least within the limits of the experiments in Table V. If the average deviation of the values of  $n$  is under 0.7%, the invertase preparation may be classified as normal; if the values of  $n$  decrease and the average deviation is much over 0.7%, then the invertase preparation is abnormal.

### VIII. Attempts to Make the Abnormal Invertase Act Normally.

There were no known differences in the method used in obtaining the normal and abnormal invertase preparations. However, it was deemed advisable to find out whether the abnormality could be due to some im-

purity which might be removed by further dialysis. Accordingly a sample of Invertase 6 was dialyzed for 3 days more in a collodion bag against running tap water. During the dialysis its volume was about doubled and its activity decreased by about  $\frac{1}{2}$  on that account; this was designated as Invertase 6B. To avoid this loss in activity, a sample of Invertase 3 was concentrated by evaporation in a collodion bag by fanning at room temperature<sup>17</sup> until it had lost about half its volume, and then dialyzed for 4 days, when it had regained about its original volume; this was designated as Invertase 3B. The results of experiments with these dialyzed preparations are given in Table IX.

TABLE IX.  
EFFECT OF DIALYSIS ON ABNORMAL INVERTASE.

Expt. B22.				Expt. B24.			
16 cc. of Invertase 6B per 100 cc.				1.903 cc. of Invertase 3B per 100 cc.			
Time, l. Min.	Rotation, degrees.	Amt. inverted, p, %.	$n \times 10^5$ .	Time, l. Min.	Rotation, degrees.	Amt. inverted, p, %.	$n \times 10^5$ .
0	13.10	0	...	0	13.05	0	...
15	11.41	10.03	476	15	11.44	9.55	453
30	9.78	19.70	477	30	9.89	18.75	453
50	7.74	31.81	476	60	7.08	35.43	446
70	5.89	42.79	473	90	4.63	49.97	442
90	4.24	52.58	470	120	2.65	61.72	435
115	2.53	62.73	464	180	-0.19	78.58	429
140	1.10	71.22	462	240	-1.77	87.95	422
180	-0.58	81.19	459	300	-2.61	92.94	412
240	-2.08	90.09	456	4 days	-3.80	Mean,	437
300	-2.83	94.54	449			Av. dev.,	2.75%.
		Mean,	466				
		Av. dev.,	1.76%.				

The decrease in the values of  $n$  and the large average deviations show that the invertase was still abnormal.

Since the abnormality could not be removed by purification by dialysis, it was thought that it might be due to the absence of some substance contained in the normal invertase. A sample of Invertase 8 was inactivated by boiling, and was proved to be totally inactive by the absence of any action on sugar solutions. Experiments were then conducted in which the solutions contained 10 cc. of this inactive invertase per 100 cc. in addition to the abnormal invertase under investigation. The results are given in Table X.

The figures in Table X indicate that the presence of boiled normal invertase caused preparation No. 3 to act normally, giving constant values of  $n$ , while it was practically without effect on preparation No. 6. This apparently means that there are different kinds of abnormality in different invertase preparations.

<sup>17</sup> Kober, THIS JOURNAL, 39, 944 (1917).

TABLE X.

EFFECT OF BOILED NORMAL INVERTASE ON THE ACTION OF ABNORMAL INVERTASE.

Expt. B25.				Expt. B26.			
10 cc. of boiled Invertase 8 and 1.905 cc. of Invertase 3 per 100 cc.				10 cc. of boiled Invertase 8 and 1.943 cc. of Invertase 3 per 100 cc.			
Time, $t$ , Min.	Rotation, degrees.	Amt. inverted, $p$ , %.	$n \times 10^4$ .	Time, $t$ , Min.	Rotation, degrees.	Amt. inverted, $p$ , %.	$n \times 10^4$ .
0	13.17	0	...	0	13.17	0	...
15	11.61	9.26	439	15	11.59	9.38	445
30	10.10	18.22	440	30	10.06	18.46	446
60	7.31	34.78	437	60	7.24	35.19	443
90	4.85	49.38	436	90	4.76	49.91	441
120	2.78	61.66	434	120	2.67	62.31	441
180	-0.19	79.29	437	180	-0.26	79.70	441
240	-1.85	89.14	440	240	-1.91	89.50	446
300	-2.68	94.07	437	300	-2.72	94.30	443
3 days	-3.68	Mean, 437		3 days	-3.71	Mean, 443	
		Av. dev., 0.34%.				Av. dev., 0.40%.	

Expts. B36 and B38.					Expts. B35 and B37.				
10.45 cc. of Invertase 6 per 100 cc.					10 cc. of boiled Invertase 8 and 10.45 cc. of Invertase 6 per 100 cc.				
Time, <i>t</i> , Min.	Rotation, B36, Degrees.	Rotation, B38, Degrees.	Amt. inverted, <i>p</i> , %.	<i>n</i> ×10 <sup>4</sup> .	Time, <i>t</i> , Min.	Rotation, B35, Degrees.	Rotation, B37, Degrees.	Amt. inverted, <i>p</i> , %.	<i>n</i> ×10 <sup>4</sup> .
0	13.14	13.13	0	...	0	13.25	13.24	.....	...
15	11.55	11.57	9.38	445	15	11.67	11.67	9.38	445
30	10.04	10.06	18.34	443	30	10.15	10.16	18.34	443
60	7.27	7.29	34.78	437	60	7.36	7.39	34.84	438
90	4.87	4.88	49.02	432	90	4.94	4.98	49.20	434
120	2.84	2.84	61.13	429	120	2.92	2.94	61.25	430
180	-0.04	-0.06	78.28	426	180	-0.01	0.04	78.52	428
240	-1.72	-1.71	88.13	424	240	-1.67	-1.64	88.43	429
300	-2.61	-2.59	93.41	422	300	-2.53	-2.50	93.53	425
3-6 days.	-3.72	-3.72	Mean,	433	2-5 das.	-3.60	-3.61	Mean,	434
Av. dev., 1.67%.					Av. dev. 1.38%.				

In order to show that preparation No. 3 had not become normal simply on standing, but that the normal course of the reaction was really produced by the presence of the boiled invertase, other experiments were run with Invertase 3 alone, and were found to give decreasing values of  $n$ , as before. These values, however, were somewhat smaller than those obtained in Expts. B12 to B15, indicating that this preparation had appreciably lost activity on being kept in the ice-box for less than 5 months.

Further experiments were made with the abnormal invertase preparations Nos. 3 and 6 in the presence of different concentrations of sodium chloride. The results are given in Table XI.

The figures in Table XI indicate that increasing concentrations of sodium chloride exert an increasing retarding effect on the action of the



TABLE XI.

EFFECT OF SODIUM CHLORIDE ON ABNORMAL INVERTASE.

Expt. B44.				Expt. B43.			
1.905 cc. of Invertase 3 per 100 cc. in 0.02 <i>M</i> NaCl.				1.905 cc. of Invertase 3 per 100 cc. in 0.05 <i>M</i> NaCl.			
Time, <i>t</i> , Min.	Rotation, degrees.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .	Time, <i>t</i> , Min.	Rotation, degrees.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .
0	13.05	.....	...	0	13.05	0	...
17	11.34	10.15	425	15	11.54	8.96	424
30	10.08	17.63	425	30	10.12	17.39	419
60	7.38	33.65	422	60	7.44	33.29	417
90	4.99	47.83	420	90	5.08	47.30	414
120	2.99	59.70	416	120	3.03	59.47	414
180	0.00	77.45	417	180	0.05	77.15	414
240	-1.73	87.72	419	240	-1.69	87.48	415
300	-2.64	93.14	416	300	-2.61	92.94	412
2-3 days	-3.80	Mean, 420		2-4 days	-3.82	Mean, 416	
		Av. dev., 0.71%.				Av. dev., 0.70%.	

Expt. B42.				Expt. B48.			
1.905 cc. of Invertase 3 per 100 cc. in 0.1 <i>M</i> NaCl.				10.45 cc. of Invertase 6 per 100 cc. in 0.1 <i>M</i> NaCl.			
Time, <i>t</i> , Min.	Rotation, degrees.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .	Time, <i>t</i> , Min.	Rotation, degrees.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .
0	13.05	0	...	0	13.13	0	...
15	11.58	8.72	413	15	11.61	9.02	427
30	10.16	17.15	413	30	10.17	17.57	423
60	7.50	32.94	410	60	7.52	33.29	417
90	5.14	46.94	410	90	5.19	47.12	412
120	3.13	58.87	408	123	3.02	60.00	408
180	0.14	76.62	408	165	0.86	72.82	407
240	-1.66	87.30	413	225	-1.17	84.87	408
300	-2.59	92.82	410	300	-2.47	92.58	405
3 days	-3.84	Mean, 411		3-6 days	-3.75	Mean, 414	
		Av. dev., 0.46%.				Av. dev., 1.67%.	

invertase. This was not observed in the work of Fales and Nelson<sup>18</sup> at the optimum hydrogen-ion concentration, but this may be due to the fact that they worked with a very much smaller sugar concentration, 0.5 g. per 100 cc. This retardation, however, seems to have more effect at the beginning of the hydrolysis than at the end in the case of Invertase 3, for in Expt. B42, with 0.1 *M* sodium chloride, the values of  $n$  were constant and the action must be classed as that of normal invertase. Invertase 6, however, was not made normal by 0.1 *M* sodium chloride, for in Expt. B48 the values of  $n$  decreased as much as ever. An experiment with 0.5 *M* sodium chloride and Invertase 6 gave values which decreased somewhat less, but still were not constant enough for the action to be regarded

<sup>18</sup> Fales and Nelson, *THIS JOURNAL*, 37, 2769 (1915).

as normal. Unfortunately the supply of Invertase 6 became too low for further experiments to be carried out with it.

Further experiments were made with Invertase 3 to determine the effect of invertase concentration on the abnormal action. The results are given in Table XII.

TABLE XII.

## ABNORMAL INVERTASE AT DIFFERENT CONCENTRATIONS.

Expts. B58 and B59.					Expts. B54 and B55.				
0.5 cc. of Invertase 3 per 100 cc.					3 cc. of Invertase 3 per 100 cc.				
Time, t, Min.	Rotation, B58, Degrees.	B59.	Amt. inverted, p, %.	$n \times 10^4$ .	Time, t, Min.	Rotation, B54, Degrees.	B55.	Amt. inverted, p, %.	$n \times 10^4$ .
0	13.05	13.05	0	...	0	13.06	13.06	0	...
60	11.53	11.51	9.08	108	10	11.46	11.48	9.44	671
120	10.06	10.05	17.80	107	20	9.96	9.98	18.34	664
195	8.35	8.33	27.95	106	30	8.52	8.55	26.88	662
270	6.72	6.77	37.45	106	45	6.50	6.53	38.87	660
360	5.06	5.06	47.42	104	70	3.62	3.67	55.91	654
450	3.50	3.54	56.56	103	100	0.98	....	71.69	654
540	2.22	2.20	64.33	102	120	-0.29	-0.28	79.23	654
1101	-1.96	....	89.08	96	150	-1.62	-1.62	87.12	656
7 to 12 days	-3.79	-3.79	Mean, 104 Av. dev., 2.7%		3 to 8 days	-3.79	-3.79	Mean, 659 Av. dev., 0.74%	

Expts. B56 and B57.				
6 cc. of Invertase 3 per 100 cc.				
Time, t, Min.	Rotation, B56, Degrees.	B57.	Amt. inverted, p, %.	$n \times 10^4$ .
0	13.12	13.12	0	...
6	11.21	11.23	11.28	134
12	9.40	9.43	22.02	134
18	7.72	7.72	32.05	133
26	5.66	5.66	44.27	133
35	3.62	3.62	56.38	132
48	1.25	1.30	70.33	132
65	-0.88	-0.84	82.97	134
85	-2.26	.....	91.28	135
4 to 5 days	-3.75	-3.74	..... Mean, 133 Av. dev., 0.67%	

These results show that in the case of Invertase 3 the abnormality decreases with increasing amount of invertase or increases with decreasing amount of invertase or increasing time of reaction.

It is not possible to explain these changes in the abnormality of Invertase 3 at the present time.

### IX. Attempts to Make Normal Invertase Become Abnormal.

Since the presence of sodium chloride had seemed to some extent to favor the normal course of invertase action, it seemed worth while to find out whether further dialysis, by removing any last traces of salt, could

make a specimen of normal invertase act abnormally. Accordingly a sample of Invertase 8 was dialyzed for a week in a collodion bag against 8 changes of distilled water. This was designated as Invertase 8A, and when tested was found to be still normal, as is shown by the results in Table XIII, Expt. B46.

Another sample of Invertase 8 was partially inactivated by heating for 1 hour on a water-bath at 50°, and then for 1/2 hour more at about 57°. This reduced its activity by about one-half. This invertase, No. 8E, was also found to be still normal, as is shown by Expts. B50 and B51, Table XII.

A further attempt to render Invertase 8 abnormal was made by exposing some of it for 2 hours, in a quartz flask, to the ultraviolet and other radiation given by a mercury arc lamp. The result, Invertase 8F, had about one-half the activity of Invertase 8, but was also found to be still normal, as is shown by Expts. B52 and B53, Table XIII.

TABLE XIII.  
ACTION OF NORMAL INVERTASE AFTER FURTHER DIALYSIS, HEATING, AND EXPOSURE TO THE MERCURY ARC.

Expt. B46.				Expts. B50 and B51.				
Invertase 8A, dialysed, 5 cc. per 100 cc.				Invertase 8E, heated, 5 cc. per 100 cc.				
Time, <i>t</i> , Min.	Rotation, Degrees.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .	Time, <i>t</i> , Min.	Rotation, B50. Degrees.	B51. Rotation, Degrees.	Amt. inverted <i>p</i> , %.	$n \times 10^4$ .
0	13.06	0	...	0	13.10	13.10	0	...
15	11.27	10.62	505	15	10.94	10.94	12.82	612
30	9.56	20.77	504	30	8.88	8.89	25.04	614
60	6.44	39.29	501	50	6.37	6.38	39.94	612
90	3.78	55.07	499	70	4.18	4.19	52.94	610
120	1.66	67.66	497	90	2.30	2.35	63.98	610
180	-1.14	84.27	501	110	0.79	0.84	72.94	612
230	-2.34	91.39	502	140	-0.87	-0.85	82.85	618
270	-2.87	94.54	499	180	-2.20	-2.18	90.74	624
3 days	-3.79	Mean,	501	2-5 days	-3.78	-3.78	Mean,	614
		Av. dev., 0.40%.					Av. dev., 0.57%.	
Expts. B52 and B53.								
Invertase 8F, exposed to mercury arc, 5 cc. per 100 cc.								
Time, <i>t</i> , Min.	B52. Rotation, Degrees.	B53. Rotation, Degrees.	Amt. inverted, <i>p</i> , %.	$n \times 10^4$ .				
0	13.09	13.09	0	...				
15	10.33	10.35	16.32	785				
25	8.61	8.63	26.53	783				
35	6.99	7.04	36.08	781				
45	5.51	5.53	44.92	779				
65	2.93	2.99	60.12	775				
85	0.94	0.97	72.05	776				
105	-0.54	-0.53	80.89	781				
140	-2.12	-2.12	90.27	787				
1 to 3 days	-3.77	-3.80	.....	Mean, 781				
				Av. dev., 0.38%.				

Since the values of  $n$  in Table XIII are constant in each experiment, having an average deviation from the mean in each case of less than 0.7%, the results show that the invertase was still acting normally. Hence it may be concluded that it is not possible by any of these three methods of treatment to render a normal invertase preparation abnormal.

### X. Experimental Details.

**Preparation of materials.**—The invertase used was all obtained from yeast by the method of Nelson and Born,<sup>19</sup> with slight modifications as described below. Preparations 6 and 7 had been made by previous workers in this laboratory and had been kept for several years in solution, saturated with toluene, in an ice-box. Preparations 1, 2 and 3 were made from yeast which had been permitted to autolyze for about a month and then filtered, and the filtrate had been treated with toluene and kept in stoppered bottles at room temperature for three years or more. During this time more solid matter had separated, and this was filtered off and the filtrate treated according to the method described by Nelson and Born<sup>14</sup> with the following modifications. Only one precipitation with alcohol was used and the kaolin treatment was omitted. After treatment with lead acetate and potassium oxalate, the filtrate was dialyzed for from 4 to 6 days in collodion bags against running tap water. The solutions become colorless and nearly clear during the dialysis. The dialyzed solutions were not precipitated again, but were preserved with toluene and kept in the ice-box until needed for the experiments. Preparation No. 8 was prepared by the same method from a new lot of 100 pounds of pressed yeast.<sup>20</sup> The preparation of Invertase No. 2 was carried out by Nelson and Simons,<sup>21</sup> who modified the treatment further by nearly neutralizing the solution with ammonia before the alcohol precipitation. No differences in the method of preparation are known which might account for the abnormality of invertase preparations Nos. 3 and 6.

Two lots of sucrose were used. In each case the starting point was the best commercial sugar, which was dissolved in distilled water and clarified with charcoal. The first lot was precipitated by alcohol by the method of Cohen and Commelin.<sup>22</sup> Its rotation was found to agree within 0.1% with that calculated from the formulas of Landolt and Schönrock.<sup>23</sup> The second lot was recrystallized from water by a procedure similar to that of Bates and Jackson.<sup>24</sup> Its rotation agreed with the calculated value within 0.04%.

Other chemicals were c. P. grades used without further purification.

<sup>19</sup> Nelson and Born, *THIS JOURNAL*, 36, 393 (1914).

<sup>20</sup> Kindly furnished by the Jacob Ruppert Brewery of New York City.

<sup>21</sup> Simons, *Dissertation*, Columbia University, 1921; Nelson and Simons, *THIS JOURNAL*, (to be published later).

<sup>22</sup> Cohen and Commelin, *Z. physik. Chem.*, 64, 29 (1908).

<sup>23</sup> Browne, "A Handbook of Sugar Analysis," John Wiley and Sons, New York, 1912, pp. 177-8.

<sup>24</sup> Bates and Jackson, *Bur. of Standards Sci. Papers*, No. 268, 75 (1916).

**Apparatus.**—Constant temperature was obtained by the use of an electrically controlled water-bath which remained at  $25^{\circ} \pm 0.01^{\circ}$ .

The progress of the inversion was followed by means of a Schmidt and Haensch polarimeter reading to  $0.01^{\circ}$ . The tubes used were 200 mm. long, and were proved to be of the same length by observing the rotation of the same 10% sugar solution in each tube. The temperature of the tubes was kept constant by the thermostat described by Nelson and Beegle,<sup>25</sup> which maintained a temperature of  $25^{\circ} \pm 0.05^{\circ}$ .

Monochromatic light of wave length  $546.1 \mu\mu$  was obtained from a mercury vapor arc by purification through two Wratten filters, one a No. 77, and the other a No. 77 which had been re-cemented with a green film in place of the yellow one. Thanks are due to Dr. C. E. K. Mees of the Eastman Kodak Company for preparing these filters. This light made it possible to use the polariscope with a half-shadow angle of  $0.5^{\circ}$ .

Nonsol bottles were used to contain the solutions undergoing hydrolysis. All volumetric apparatus used in making up solutions was calibrated.

**Control of the Hydrogen-ion Concentration.**—The desired hydrogen-ion concentration was obtained by the use of a buffer mixture of 0.1 *M* acetic acid and 0.1 *M* sodium acetate in the proportions given by Michaelis.<sup>26</sup> One hundred cc. of the final solution always contained 10 cc. of this buffer, making the total concentration 0.01 *M*. This concentration was low enough so that any salt effect on the invertase action was negligible, especially at the optimum hydrogen-ion concentration.<sup>18</sup> In the experiments of Nelson and Vosburgh<sup>1</sup> the desired hydrogen-ion concentration was obtained by the use of diluted hydrochloric acid. In the experiments of Vosburgh and Nelson<sup>14</sup> a buffer of citric acid and secondary sodium citrate was used at a total citrate concentration of 0.01 *M*.

The hydrogen-ion concentration was measured during or after each inversion by the colorimetric method of Sørensen,<sup>15</sup> using  $\alpha$ -naphthyl-amino-azo-*p*-benzene sulfonic acid as indicator with citrate standards. The latter were standardized electrometrically with the hydrogen electrode and the saturated potassium chloride calomel cell<sup>27</sup> using a salt bridge of saturated potassium chloride solution. The hydrogen-ion concentrations were based on 0.1000 *M* hydrochloric acid as a standard, its ionization<sup>28</sup> being taken as 92.04% at  $25^{\circ}$ , the temperature at which the present determinations were made.

**Procedure.**—In general the procedure followed was that recommended by Vosburgh.<sup>16</sup> Duplicate experiments were run on different days with freshly prepared sugar solutions. A solution was made up containing

<sup>25</sup> Nelson and Beegle, *THIS JOURNAL*, **41**, 559 (1919).

<sup>26</sup> Michaelis, "Die Wasserstoffionenkonzentration," Springer, Berlin, 1914, p. 184.

<sup>27</sup> Fales and Mudge, *THIS JOURNAL*, **42**, 2434 (1920).

<sup>28</sup> Fales and Vosburgh, *ibid.*, **40**, 1295 (1918).

sucrose and buffer in such concentrations that when a certain volume of this had been measured out it would be possible to add from a pipet a round number of cubic centimeters of invertase to start the reaction. For example, in Expt. B1 32.680 g. of sucrose and 32.68 cc. of buffer were diluted to 500 cc. at 25°. Of this solution 321.80 cc. was pipetted into a Nonsol bottle, and 5 cc. of invertase was added to start the reaction. This produced the initial concentrations given in Table I A. The solutions were stirred by a current of filtered air while being mixed, and samples were taken by pipets delivering in 10 seconds or less.<sup>21</sup> The time of mixing or of sampling was taken as the mean time of delivery of the pipet used. The reaction was stopped and mutarotation hastened by the use of sodium carbonate as recommended by Hudson,<sup>29</sup> a 25cc. sample being added to 5 cc. of 0.1 *M* sodium carbonate solution. The initial rotation of each solution was determined by preparing samples of identical composition in which the sodium carbonate was added to the sugar before the addition of the invertase, thus rendering the invertase entirely inactive. The rotation of each solution was determined by taking the mean of at least four concordant readings, the tube being rotated slightly after each reading to ensure the detection of any strain in the cover glasses.<sup>30</sup> The zero point of the polariscope was similarly determined by the use of a tube filled with distilled water. The final rotations were obtained by taking samples 2 days or more after the start of the reaction. Samples taken on the second and third days usually had the same rotation. In calculating the percentage inverted, the total change in rotation was always taken as 16.85°, since this value was obtained in all the experiments of Vosburgh and Nelson<sup>14</sup> as well as in the majority of the present experiments.

Since in several experiments the total change in rotation appeared to be a few hundredths of a degree more than 16.85°, it was thought advisable to test the effect of such differences on the values of  $n$  as obtained by the use of Equation 12. A sample calculation was made for Expt. B46, Table XIII, with the following results.

Using 16.85°, $n \times 10^4$ .		Using 16.89°, $n \times 10^4$ .	
505	501	504	498
504	502	503	497
501	499	500	492
499	Mean, 501	497	Mean, 498
497	Av. dev., 0.40%	495	Av. dev., 0.60%.

These results show that an error of 0.04° in determining the total change in rotation could not have caused sufficient error in the values of  $n$  to make a normal invertase preparation appear abnormal. Since this was the

<sup>29</sup> Hudson, *THIS JOURNAL*, 30, 1564 (1908).

<sup>30</sup> Browne, *Ref. 23*, p. 156.

extreme deviation noticed from the value  $16.85^\circ$ , the procedure adopted of taking the total change as  $16.85^\circ$  in all calculations is quite justified.

A calculation of the possible error in determining the rotation of any sample which might be due to errors in the various measurements of weight and volume involved in this procedure has been made by Messrs. G. Bloomfield and F. Hollander of this laboratory. Using estimates of these errors based on the present authors' calibrations, this calculation gave a maximum error of about  $0.01^\circ$  in the determination of the rotation of a sample. Since the duplicate experiments did not always agree so well as this, a fairer estimate of the precision of the measurements may be obtained from the agreement of the duplicates themselves. This would put the average difference between duplicate measurements of a change in rotation at about  $0.02^\circ$ . The effect of such an error on the values of  $n$  obtained by the use of Equation 12 has already been considered.

### Summary.

1. It has been shown that not all preparations of yeast invertase are alike in their action, but that some are abnormal in allowing the hydrolysis of cane sugar to slow up more than others after the first 20% of the inversion.
2. An empirical equation is given which fits the hydrolysis of cane sugar by normal invertase over an extreme range of invertase concentration of 12:1. By this means it has been shown that the hydrolysis-time curves for normal invertase are of the same shape for these different invertase concentrations and can be made to superimpose if the time scale be multiplied by the proper constant.
3. By the same method it has been shown that the hydrolysis curve with normal invertase has the same shape at temperatures varying from  $15^\circ$  to  $35^\circ$ , and at hydrogen-ion concentrations from  $4.0 \times 10^{-6}$  to  $3.2 \times 10^{-7}$ .
4. It was found that one abnormal invertase preparation could be rendered normal by the presence of boiled normal invertase or 0.1 *M* sodium chloride, while another was not affected by either. The former preparation also worked normally at a very high concentration.
5. It was found impossible to render a normal invertase preparation abnormal by further dialysis or partial inactivation by heating or ultra-violet light.

The authors are glad to acknowledge their indebtedness to the Harriman Research Laboratory, New York City, for financial assistance in this investigation.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE OREGON EXPERIMENT STATION.]

## NITROGEN COMPOUNDS IN ALFALFA HAY.

BY HARRY G. MILLER.

Received August 22, 1921.

In an earlier paper results were reported on the distribution of nitrogen in the alfalfa seed. A similar study has now been made on a sample of alfalfa hay, although this phase of the investigation was begun before the work on nitrogen distribution in the seed was undertaken. The difficulty of separating the nitrogen compounds in the alfalfa hay prompted the writer to apply certain analytical methods to the seed to obtain information as to what nitrogen compounds might be present in the leaves and stems of the alfalfa plant. Results of the study to ascertain the nitrogen groups in alfalfa hay, while not complete, are reported in this paper, due to a discontinuance of this work for a year.

The sample of hay was grown in eastern Oregon and was cut at a time when the hay, according to agricultural practice, is best suited for feeding purposes. It contained 1.98% of nitrogen. Extracting 25 g. of finely ground alfalfa with ether followed by alcohol and then water in a Soxhlet extractor removed the following amounts of nitrogen given as percentages of the total nitrogen; ether, 0.85%; alcohol (95%), 5.32%; and water, 34.5%. In all 40.7% of the total nitrogen was removed. The residue from extraction weighed 15.71 g. and contained 1.86% of nitrogen. By difference, the solids dissolved would weigh 9.29 g. and contain 2.18% of nitrogen. In cold water 39.0% of the total nitrogen was soluble, 10% sodium chloride solution extracted an additional 9.8% and this followed by 0.2% potassium hydroxide solution brought the total up to 58.1%. Extracting directly with 0.2% potassium hydroxide solution removed 58% of the nitrogen of which 53% was precipitated with acetic acid leaving 27.3% of the total nitrogen in solution. Hot water extraction removed 28.7%; however, when this residue was further extracted with the potassium hydroxide solution only 4.5% of the total nitrogen was brought into solution compared to about 31% before. Heating the residue to the boiling point of water apparently changed the nature of the alkali-soluble nitrogen compounds. A 0.5% potassium hydroxide solution extracted more nitrogen from alfalfa which had been ground fine enough to pass through a 40-mesh sieve than from ordinary chopped alfalfa for feeding purposes. After the proteins were removed from these extracts the nitrogen content of the filtrates was the same, representing 27.7% of the total nitrogen. As an example 4 g. each of coarse and fine alfalfa were extracted with 0.5% potassium hydroxide solution; the total amounts of nitrogen extracted were 0.0325 g. and 0.0465 g. respectively. The weights of nitrogen precipitated as protein were 0.0111 g. from the coarse material and



0.0246 g. from the finely ground sample, leaving as non-protein 0.0214 g. and 0.0219 g., respectively. A cold-water extract of the fine material after removing the protein with acetic acid contained 28% of the total nitrogen, while a hot-water extract of the coarse alfalfa contained 27.8% of the nitrogen. Apparently there are certain nitrogen compounds which are very easily extracted with hot water, cold water or alkali, and after removing the protein from the two latter solutions the percentages of non-protein nitrogen extracted are the same regardless of the degree of fineness of the alfalfa. Alkali extracted about 100% more protein from the finer particles than from the chopped alfalfa.

Mixing the alfalfa flour with water and 0.5% potassium hydroxide solution and placing the sealed containers in a freezing mixture of ice and salt ( $-20^{\circ}$ ) did not cause more nitrogen to be extracted, but rather less; the water solution contained 29.2% of the total nitrogen and the alkali extract 40.8%. Subjecting a 3g. sample of alfalfa to the crude fiber determination did not extract all of the nitrogen, as 7.3% still remained. The dilute sulfuric acid (1.25%) removed only 8.5%, while the following sodium hydroxide solution (1.25%) extracted 49.1%. The preceding extraction with ether and water removed 0.9% and 30% nitrogen, respectively. The 4.2% not accounted for was most probably removed as ammonia in the sodium hydroxide digestion.

### Protein Nitrogen.

A preparation of protein for applying the Van Slyke method to determine certain nitrogen groups was obtained by extracting the alfalfa with 0.5% potassium hydroxide solution. Nearly all the extract was obtained by using a press. The solution after filtering was acidified with either acetic or hydrochloric acid to precipitate the protein. The protein was then extracted with absolute alcohol in a Soxhlet extractor until the extract was practically colorless, the alcohol was washed out with ether and the protein dried in a vacuum desiccator over sulfuric acid. Analysis showed for nitrogen, 12.9%; for sulfur, 0.85%; and for ash, 1.27%. No preparation of protein contained over 13% of nitrogen in spite of repeated precipitation and thorough alcohol extraction. After the protein was dried it would not dissolve in alkali in the cold and only with difficulty in an alcoholic-alkali solution (50.0 cc. of alcohol+50 cc. of 1% potassium hydroxide solution). Decomposition of the protein took place in the latter process.

After this work had been completed, Dowell and Menaul<sup>1</sup> reported results on nitrogen distribution of some proteins obtained by dilute alkali extraction. The protein they obtained from alfalfa contained 13.6% nitrogen ( $0.85 \times 0.16$ ). Chibnall and Schryver<sup>2</sup> obtained proteins from the green leaves of cabbage, spinach, bean, grass, etc., by extracting with water, using ether as a cytolytic agent. Their products sepa-

<sup>1</sup> Dowell and Menaul, *J. Biol. Chem.*, **46**, 437 (1921).

<sup>2</sup> Chibnall and Schryver, *Biochem. J.*, **15**, 60 (1921).

rated on warming this solution to 40°. When freshly prepared they were soluble in weak alkaline solutions from which they could be precipitated by acids. They contained about 13% of nitrogen. A protein preparation obtained by Osborne and Wakeman<sup>3</sup> from green spinach leaves contained 15.3% of nitrogen. They ground the fresh leaves with water, centrifuged out the cellular matter, after which they precipitated a substance containing 14% nitrogen. This was brought into solution with alkali and another precipitate obtained by adding acid which contained 15.3% nitrogen. This corresponds more nearly to nitrogen content of protein from seeds while in the results reported from the other workers the nitrogen content of the proteins in the leaves averages about 13.0%.

Results of analysis of the protein by the Van Slyke method are given in the following table. Two portions of Sample I weighing 3.2856 g. and 3.6353 g., equivalent to 0.4230 and 0.4681 g. of nitrogen, were hydrolyzed for 20 hours with 20% hydrochloric acid; 3.31 g. of Sample II, containing 0.4145 g. of nitrogen, was hydrolyzed for 30 hours. The percentage nitrogen distribution of the protein of the seed reported in an earlier paper<sup>1</sup> is given in the last column for comparison. So far as the writer knows there are no other data showing a comparison of the nitrogen distribution between a seed protein and the protein existing in the stems and leaves of the same plant, both obtained by the same method.

TABLE I.  
ANALYSIS OF PROTEIN FROM ALFALFA HAY BY THE VAN SLYKE METHOD.

Form of Nitrogen.	Sample I.				Sample II.		Protein from Seed.	
	G.	a.	b.	%.	G.	%.	Av. %.	Av. %.
Amide.....	0.0266	6.15	0.0280	5.98	0.0266	6.41	6.18	8.67
Humin, adsorbed by lime.....	0.0227	5.36	0.0210	4.49	0.0211	5.09	6.11 <sup>a</sup>	4.41
Humin, insoluble in amyl alcohol....	0.0005	0.01	0.0025	0.53	0.0017	0.40	.....	.....
Humin, in amyl alcohol extract....	0.0032	0.75	0.0062	1.32	0.0015	0.38	.....	.....
Arginine.....	0.0585	13.83	0.0625	13.25	0.0592	14.28	13.82	21.38
Histidine.....	0.0110	2.60	0.0170	3.63	0.0156	3.76	3.33	5.42
Lysine.....	0.0525	12.41	0.0493	10.53	0.0422	10.18	11.04	6.11
Cystine.....	0.0040	0.95	0.0039	0.90	0.0040	0.90	0.91	1.01
Amino, filtrate....	0.2345	55.44	0.2603	55.61	0.2358	56.88	55.98	47.87
Non-amino, filtrate.	0.0096	2.27	0.0096	2.05	0.0117	2.82	2.38	5.32
Total recovered <sup>b</sup> ...	0.4231	99.77	0.4603	98.39	0.4192	101.10	99.75	100.19

<sup>a</sup> Average of the three different forms of humin nitrogen.

<sup>b</sup> Total nitrogen corrected for solubility of bases.<sup>4</sup>

An explanation as to why the nitrogen content of the leaf protein (13.0%) was lower than that of seed protein (15.6%) may be found in these data. The protein from the seed yielded a larger quantity of the basic amino acids

<sup>3</sup> Osborne and Wakeman, *J. Biol. Chem.*, 42, 1 (1920).

<sup>4</sup> Plimmer, "The Chemical Constitution of the Proteins. I. Analysis," Longmans, Green and Company, 1917, p. 107.

than the leaf protein; especially is this significant in the arginine content of the two proteins. Calculating the weight of arginine present from the above nitrogen distribution, 1 g. of seed protein contains 0.1032 g. of arginine, while the same weight of leaf protein contains 0.0558 g. of arginine. As arginine contains more nitrogen than any other amino acid thus far isolated, its replacing other amino acid groups in the protein molecule or direct addition to the same would increase the nitrogen content of the protein. Of course low arginine content does not mean low nitrogen content of the protein or *vice versa*, which is shown in tables<sup>5</sup> giving the nitrogen distribution in proteins. However, as further evidence will be given, analytical results show that there is an increase in concentration of the arginine group to total nitrogen as the nitrogen compounds pass from the leaves into the seed and this may explain the higher nitrogen content of the seed protein over the leaf protein. Distribution of nitrogen in the hydrolytic products of the whole alfalfa seed reported in the earlier paper<sup>6</sup> shows that 14.98% of the total nitrogen reacted as arginine nitrogen, and that this could all be calculated as coming from the protein present in the seed. Grindley, Joseph and Slater<sup>7</sup> report 7.68% arginine in the hydrolytic products of alfalfa hay. This compared with the arginine content of the seed shows the large difference in arginine concentration. In the Van Slyke method of determining arginine in the hydrolytic products of alfalfa hay and the whole seeds there may be other nitrogen compounds present liberating ammonia when boiled with the alkali solution, thus giving a higher arginine content than the actual amount present. This does not appear to be the case with alfalfa seed for reasons already mentioned. With hay this undoubtedly takes place as will be shown later in the discussion of the water-soluble nitrogen compounds, which would make the difference between the actual ratio of arginine to total nitrogen greater than the above figures show. Roxas<sup>8</sup> found that arginine gave up 2.3% of its nitrogen for humin formation; this reaction would have a tendency to lower the actual arginine nitrogen in the solution, although it should not interfere seriously with the above results.

Chibnall and Schryver<sup>2</sup> state that the protein isolated from cabbage was acidic in properties and on hydrolysis yielded an amount of ammonia corresponding to 5% of the total nitrogen. They comment as follows: "These results indicate that acidic proteins exist in the leaves, which when they pass into the resting stage in the seed, undergo amidization. Such proteins should contain a relatively small amount of nitrogen." The higher percentage of amide nitrogen in the seed protein compared to the

<sup>5</sup> Ref. 4, p. 107.

<sup>6</sup> Miller, *THIS JOURNAL*, 43, 906 (1921).

<sup>7</sup> Grindley, Joseph and Slater, *ibid.*, 37, 1778 (1915).

<sup>8</sup> Roxas, *J. Biol. Chem.*, 27, 71 (1916).

leaf protein recorded in the above table gives support to this view. It appears logical to assume from the presence of these groups with a high nitrogen concentration in the seed protein and the appreciable quantities of ammonium salts and other soluble nitrogen compounds in the green plant that as the plant matures these simple nitrogen compounds are gradually incorporated into the protein molecule, thus increasing the nitrogen content of the latter. The spinach used by Osborne and Wakeman may have reached a more advanced stage of maturity than the sample used by Chibnall and Schryver and on the above assumption should contain more nitrogen. No study has yet been made pertaining to the equilibrium existing between ammonium salts, amino acids and proteins during different stages of growth. A study of this kind would help solve the problem. The possibility of the leaf protein being combined with a nitrogen-poor prosthetic group must not be overlooked and the larger yield of humin nitrogen from the leaf protein may be due to a group of this nature. The percentage distribution of the nitrogen groups in the protein from alfalfa obtained by Dowell and Menaul<sup>1</sup> varies somewhat from our results. This is probably due to a different compound, the difference being caused by the isolation of the protein at a different stage of growth.

#### The Water-Soluble Nitrogen Compounds.

As indicated before there was a certain class of nitrogen compounds, not protein, easily extracted with hot water, cold water or dil. alkali. Little is known of the nature of these non-protein nitrogen compounds. Hart and Bently,<sup>9</sup> in their work on the character of water soluble nitrogen compounds in feeding stuffs determined the ammonia nitrogen, amide nitrogen and amino nitrogen. Steenbock<sup>10</sup> isolated stachydrin from a hot-water extract of alfalfa hay. Following the same method the writer was unable to obtain any stachydrin hydrochloride from the sample of alfalfa hay used in this investigation. In removing the purines by precipitating with silver nitrate in dil. nitric acid solution a heavy flocculent precipitate formed. A similar precipitate formed with silver nitrate in an ammoniacal solution. A portion of the solution obtained from the phosphotungstic acid precipitate of the water extract of alfalfa, which reacted strongly alkaline, was slightly acidified with nitric acid and 5% silver nitrate added until a test portion gave a brown precipitate with barium hydroxide. The resulting precipitate was filtered off, washed and suspended in warm water. Hydrogen sulfide was passed in to remove the silver as silver sulfide, and the filtrate was boiled to remove excess of hydrogen sulfide. A portion of this filtrate did not give the color reaction for the murexide test. Adenine and hypoxanthine do not respond to this test.<sup>11</sup> A portion of the solid obtained by allowing

<sup>9</sup> Hart and Bentley, *J. Biol. Chem.*, 22, 477 (1915).

<sup>10</sup> Steenbock, *ibid.*, 35, 1 (1918).

<sup>11</sup> Walter Jones, "Nucleic Acids," Longmans, Green and Company, 1914, pp. 89, 95.

the above filtrate to evaporate gave the characteristic ruby-red coloration with hydrochloric acid, zinc and sodium hydroxide.<sup>12</sup> Hypoxanthine and adenine give this test. A purine precipitate was obtained again by precipitating with small quantities of solid silver sulfate in the solution slightly acidified with sulfuric acid. The sulfuric acid alone gave no precipitate, so that the alkalinity of the solution or the carbon dioxide evolved could not be attributed to the presence of barium hydroxide or carbonate not removed. The silver precipitate was suspended in water to which a few drops of hydrochloric acid were added. This solution was made ammoniacal, the precipitate filtered off and thoroughly washed. It was then suspended in nitric acid, 1.10 sp. gr., and boiled. Particles of silver chloride were filtered off and the filtrate was allowed to stand for 24 hours. Small orange colored crystals separated, weighing 0.0780 g. and containing 23.50% of nitrogen. Nitrogen calculated in the hypoxanthine salt of silver nitrate corresponding to the formula  $C_5H_4ON_4 \cdot AgNO_3$  is 22.88%.

Aeration of water extract of alfalfa removed ammonia equal to 2.0% of the total nitrogen. After hydrolyzing with 10% hydrochloric acid for 10 hours, the clear extract, after filtering off the humin nitrogen, yielded ammonia nitrogen by aeration equal to 3.75% of the total nitrogen, and amino nitrogen equivalent to 14.0% of the total nitrogen.

In preparing the phosphotungstic precipitates used in this work, the quantity of the acid required to precipitate the basic nitrogenous compounds was exceedingly great when compared to the amount required in the hydrolyzed solution of the protein. A quantity of extract containing 0.4287 g. of nitrogen was hydrolyzed with 10% hydrochloric acid for 10 hours. This was then treated in the same way as in the Van Slyke method of protein analysis. Fifteen g. of phosphotungstic acid which precipitates the basic amino acids from protein containing the same amount of nitrogen did not precipitate all the compounds that form precipitates with the acid from this hydrolyzed water extract. A further addition of 200 cc. (15 g. of phosphotungstic acid per 100 cc.) did not precipitate all the above compounds after 48 hours' standing. The precipitates formed by further separate additions of two 50cc. quantities were filtered off and the total nitrogen determined. The first contained 6.16 mg. of nitrogen, and the second 5.0 mg. These results show what small proportions of nitrogen, the nature of which permits its precipitation by phosphotungstic acid, are removed by a large quantity of the acid, especially when compared to a hydrolyzed protein solution.

The residues obtained from decomposing the phosphotungstate precipitates with barium hydroxide and removing the excess of barium, as

<sup>12</sup> Allen, "Commercial Organic Analysis," P. Blakiston's Son and Co., 1913, Vol. 7, p. 335.

the carbonate never contained over 3.5% nitrogen. Using a similar water extract made alkaline with sodium carbonate, and adding mercuric chloride solution, a precipitate was obtained, which, after removing the mercury with hydrogen sulfide and evaporating the solution to dryness, left a residue containing 13% nitrogen. The high concentration of nitrogen in the residue from the mercury precipitation was partly due to ammonium salts. The phosphotungstic precipitate was decomposed in an alkaline solution and later heated when the carbon dioxide was passed in. This process would free the ammonia while the mercury precipitate was decomposed in an acid solution.

In order to compare the mercuric chloride and phosphotungstic acid precipitations, 1000 cc. of water extract from 200 g. of alfalfa hay was treated with a 20% lead acetate solution until no further precipitate formed. Excess of lead in the filtrate was removed by adding sodium carbonate in excess. After filtering off the lead carbonate this alkaline solution was heated in a water-bath in an evaporating dish for 12 hours to drive off the ammonia, and made up to 1000 cc. To a 200cc. portion, 20 g. of mercuric chloride was added and the mixture warmed to dissolve all the chloride. Another 200cc. portion was acidified with sulfuric acid to 5% strength and 200 cc. of a 20% phosphotungstic acid solution in 5% sulfuric acid was added. After 24 hours the precipitates were decomposed in the usual way. The mercury precipitate dissolved in dil. hydrochloric acid with the formation of a white crystalline salt which contained no nitrogen and was filtered off before the hydrogen sulfide was passed in. The residue from the mercury precipitate weighed 0.79 g. and contained 8.83% of nitrogen; the phosphotungstic acid residue weighed 1.02 g. and contained 3.3% of nitrogen. Time did not permit a comparison of the total quantity of nitrogen removed when phosphotungstic acid was added until no further precipitate formed. Excess of mercury was present in the above precipitation.

The precipitate formed by the addition of lead acetate was decomposed with dil. sulfuric acid and the total nitrogen determined in the filtrate from lead sulfate; 2.75% of the total nitrogen in alfalfa or 9.82% of the non-protein nitrogen was precipitated by lead acetate. Twenty per cent. of the nitrogen from the lead precipitate was given off as ammonia when boiled with 25% potassium hydroxide, which, calculated as arginine nitrogen, would be 40% of the nitrogen in the lead precipitate. The mercury precipitate contained 8.88% of the total nitrogen. The residue from the mercury precipitate was dissolved in water and the total nitrogen determined on precipitates obtained by adding silver sulfate to the solution slightly acidified with sulfuric acid, and when it was rendered alkaline with barium hydroxide. The purine fraction contained 36% of the total nitrogen and the histidine-arginine fraction 35%; 3.2% of the total nitrogen

was in the purine fraction. Whether all of this fraction is composed of purines would have to be determined by analysis; this amount of nitrogen separated in the purine fraction by following the analytical procedure recommended.<sup>13</sup> The presence of these purines would increase the percentage of arginine as determined by the Van Slyke method on hydrolyzing the whole alfalfa hay. This was pointed out by Brewster and Alsberg<sup>14</sup> in their work with yeast nucleic acid.

### Summary.

1. Certain non-protein nitrogen compounds composing about 28% of the total nitrogen were easily extracted with water regardless of the degree of fineness of the alfalfa hay.

2. Alkali extracted more protein from the finely ground material than from the coarse.

3. The protein from alfalfa hay extracted by dilute alkali, had a nitrogen content of 13.0% and contained the basic amino acids arginine, histidine, lysine and cystine.

4. The protein from the seed yielded larger quantities of arginine and amide nitrogen than the leaf protein, which may account for the difference in the total nitrogen of the two proteins.

5. The purine fraction contained 3.2% of the total nitrogen. A crystalline salt corresponding to the nitrogen content of hypoxanthine silver nitrate was obtained.

6. Mercuric chloride precipitation of the water extract gave a residue high in nitrogen after removing the mercury, apparently suitable for further investigation pertaining to the nitrogen compounds in alfalfa hay.

CORVALLIS, OREGON.

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<sup>13</sup> Barger, "The Simpler Natural Bases," Longmans, Green and Company, 1914, p. 120.

<sup>14</sup> Brewster and Alsberg, *J. Biol. Chem.*, 37, 367 (1919).

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY, OHIO STATE UNIVERSITY.]

## CASTOR BEAN LIPASE, ITS PREPARATION AND SOME OF ITS PROPERTIES.

BY D. E. HALEY AND J. F. LYMAN.

Received August 25, 1921.

In the extended studies on lipases by Falk<sup>1</sup> and his associates little attention has been given to the most favorable conditions for the preparation and activity of the enzyme material. Taylor,<sup>2</sup> von Hoyer,<sup>3</sup> Jalander,<sup>4</sup> Tanaka,<sup>5</sup> Barton<sup>6</sup> and others have proposed methods of preparing and using castor bean lipase. In an attempt to study the action of castor bean lipase on various esters we encountered difficulties, first, in obtaining an active, approximately fat-free preparation which would act as a good emulsifying agent for water and fats; and second, in adjusting the conditions so that rapid and nearly complete hydrolysis of the fat might occur.

We have found that it is comparatively easy to overcome both of these difficulties; but, as far as we have been able to find, no one has yet described methods that can be followed with entire satisfaction.

### Preparation of Lipase Material from the Castor Bean.

An attempt was made to modify the procedure of von Hoyer with the hope of obtaining a very active lipase, free from fat and cell residues. Lipase "cream" was prepared by the method described by von Hoyer.<sup>3</sup> This was dried at room temperature and extracted with ethyl ether. The small residue insoluble in ether is designated "cream residue." A sediment which settled from the castor bean "milk" was also separated, dried and extracted with ether. The main portion, representing the cell walls and other insoluble constituents of the beans, was likewise dried and extracted. There were thus three fractions: (1) fat-free residue from castor bean "cream," (2) fat-free sediment from castor bean "milk," and (3) fat-free residue of cellular materials not emulsified or dissolved by grinding and mixing the beans with water. A comparative test for lipolytic activity showed that Fraction 3 was high in lipase, while the small residue from the "cream" contained relatively little enzyme.

The materials were mixed in test-tubes in the amount and order named; 0.1 g. of lipase preparation, 1.0 g. of olive oil and 0.6 cc. of 0.1 *N* acetic acid. The tests were incubated at 38° for 12 hours and the free fatty acids then determined by titration against 0.1 *N* alcoholic sodium hydroxide using phenolphthalein as indicator. Before making the titrations the contents of the tubes were transferred to flasks by means

<sup>1</sup> Falk and Nelson, *THIS JOURNAL*, 34, 735 (1912).

<sup>2</sup> Taylor, *J. Biol. Chem.*, 2, 87 (1906).

<sup>3</sup> von Hoyer, *Z. physiol. Chem.*, 50, 414 (1906).

<sup>4</sup> Jalander, *Biochem. Z.*, 36, 435 (1911).

<sup>5</sup> Tanaka, *J. Coll. Eng. Imp. Univ. Tokyo*, 5, 125 (1912).

<sup>6</sup> Barton, *THIS JOURNAL*, 42, 620 (1920).



TABLE I.

RELATIVE LIPOLYTIC ACTIVITY OF FAT-FREE RESIDUE FROM VON HOYER'S CASTOR BEAN "CREAM," SEDIMENT FROM CASTOR BEAN "MILK" AND MAIN INSOLUBLE RESIDUE.

Fraction.	Extent of Hydrolysis.	
	0.1 N NaOH. Cc.	%.
"Cream" residue.....	18.0	53
"Milk" sediment.....	23.6	69
Main residue.....	22.8	67

of 50 cc. of neutral alcohol. Without the alcohol satisfactory results cannot be obtained on account of hydrolysis of sodium soaps formed in the titration and also because of the insolubility of the fatty acids in water. All tests reported in this paper were made in duplicate. Corrections were made for reagents and "blank" digestions.

Since the fat-free residue from the "cream" was small and its lipolytic action relatively low, this material does not seem promising. The main residue is easily obtained in quantity and has a good degree of activity. Its physical condition is likely to be unfavorable, however, because on drying there is a tendency for it to assume a tough horny consistency; and in this condition it does not mix readily with water, nor act as a good emulsifying agent. Alcohol and acetone were tried as dehydrating agents. While they gave a lipase material of good physical condition, the lipolytic action was entirely destroyed or lost in the process. It is probable that alcohol and acetone are destructive to castor bean lipase.<sup>4</sup>

The most satisfactory lipase material that we have prepared, judging by its physical condition and by its activity in hydrolyzing fats, was obtained by a slight modification of Taylor's<sup>2</sup> method. Castor beans<sup>7</sup> are shelled by cracking the hull with a small hammer and peeling off the outer covering of the seed by hand. The kernels are ground as finely as possible in a food chopper, and extracted in a Soxhlet extractor with petroleum ether. The extracted material is then passed through a 40-mesh sieve. We have found low-boiling petroleum ether more satisfactory as a solvent for this purpose than ethyl ether, although the latter can be used. We have not attempted to concentrate or isolate the lipase from the fat-free kernels.

#### The Solubility of Castor Bean Lipase in Ether and in Ether-Fat Mixtures.

Taylor<sup>2</sup> states that lipase of castor beans is insoluble in ethyl ether but that it dissolves in a mixture of ether and fat. The following experiment tends to verify this statement. Four portions of 3 g. each of extracted bean powder were treated as follows: (1) 25 cc. of olive oil was added; (2) 25 cc. of olive oil and 100 cc. of ethyl ether were added; (3) 100 cc. of ethyl ether was added; (4) nothing was added. All were allowed to stand at room temperature for 4 days. The solvents were then removed by decantation and filtration and all 4 residues extracted with petroleum

<sup>7</sup> The castor beans were donated by the Baker Castor Oil Co., N. Y.

<sup>8</sup> Kita, *J. Chem. Ind. Tokyo*, 21, 1-5 (1918).

# CASTOR BEAN LIPASE.

If the acid is added to the enzyme material before the oil a complete loss of lipase is likely to occur. Barton<sup>6</sup> notes the better emulsion obtained when the oil is added to the enzyme material before the acid is introduced. This is undoubtedly an important point, but the danger of destroying the active enzyme by acid in the absence of fat is a more serious consideration.

## The Concentration of Acid Most Favorable to the Hydrolysis of Fats by Castor Bean Lipase.

Although many experiments have been performed to determine the effect of acid on castor bean lipase we are not aware that the most favorable concentration, expressed in terms of actual acidity, has been determined. Barton's<sup>6</sup> conclusion that castor bean lipase has its optimum activity toward the three substances, lard, olive oil and ethyl butyrate at approximately 0.6% concentration of hydrochloric acid seems quite unjustified by his own data and in entire conflict with our results. We have repeated some of Barton's experiments and, under the conditions of his tests, find little if any activity. In view of the uncertainty of the accuracy of corrections made for "blank" experiments, small digestion values appear to us to have little significance. This is borne out by the fact that negative values were obtained in many of Barton's experiments. Table IV gives the lipolytic activity of our preparation at the acid concentrations used by Barton and for comparison his results obtained under similar conditions.

TABLE IV.

### EFFECT OF VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID ON CASTOR BEAN LIPASE IN HYDROLYZING OLIVE OIL.

In each experiment 0.2 g. of lipase powder, 0.3 cc. of olive oil and 25 cc. of the acid called for were mixed and incubated at 38° for 24 hours.

Concentration HCl added, %.	Amount of Hydrolysis Produced in Terms of 0.1 N NaOH. Cc.	As found by Barton. Cc.
0.0	0.7	0.2
0.1	0.8	2.0
0.2	0.7	1.2
0.3	0.5	1.1
0.4	0.6	1.3
0.5	0.7	1.6
0.6	0.5	-0.8
0.7	0.5	-0.8
0.8	0.5	-0.1
0.9	0.5	-0.5
1.0	0.5	-0.5

It occurred to us that Barton overstepped the optimum acidity in the lowest acidity, *viz.*, 0.1% of hydrochloric acid, that he used, since in his most active mixtures the amount of fat hydrolysis was very low. Accordingly we made the following experiment to find the effect of varying the concentration of acid between 0.0 and 0.1%. At the same time we

made another series of tests in which we added the same *strengths* of acid but used much smaller volumes. The following table shows the results.

TABLE V.

EFFECT OF VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID ON CASTOR BEAN LIPASE IN HYDROLYZING OLIVE OIL.

In Series A 0.2 g. of lipase powder, 0.3 cc. of olive oil and 25 cc. of acid were mixed as described by Barton. In Series B, 0.1 g. of lipase, 1.0 g. of olive oil and 0.6 cc. of acid were mixed. The essential difference in the two series is the *amount* of acid used.

Extent of Fat Hydrolysis.					
Series A.			Series. B.		
HCl Added.	0.1 N NaOH		0.1 N NaOH		
%.	Cc.	%.	Cc.	%.	Cc.
0.00	0.7	7	1.0		3
0.02	7.4	77	2.2		6
0.04	3.9	43	16.5		49
0.06	1.1	12	18.2		54
0.08	0.7	7	24.6		73
0.10	0.8	8	24.6		73
0.12	0.6	6	27.2		79
0.14	0.3	3	30.6		90
1.16	0.1	1	29.7		88
0.18	0.3	3	28.3		84
0.20	0.3	3	27.6		81

Table V shows that whether large or small volumes of acid are used the enzyme shows its maximum activity at a certain concentration and then falls off, rapidly when the volume of acid is large and slowly when it is small. At a concentration of hydrochloric acid of 0.1% in Series A there was practically no digestion. The slight hydrolysis indicated is probably without significance and within the limit of experimental error. It must be remembered that the amount of fat used in this series was small, only 0.3 cc., and the necessary corrections for blanks, etc., were relatively large. It is to be expected that the proteins and salts of the lipase powder would show a buffer effect, and hence that the actual concentration of acid in two tubes containing equal amounts of lipase material to which different volumes of the same strength acid had been added would be different. From Table V it appears that the optimum activity in Series A is about 0.02% of hydrochloric acid, while in Series B the optimum concentration is at 0.14. It was suspected that the actual hydrogen-ion concentrations in these two mixtures were about the same. A determination was made by the colorimetric method of Clark and Lubs<sup>9</sup> as follows. Lipase powder and hydrochloric acid were mixed in the following proportions: (1) 0.2 g. of lipase to 25 cc. of 0.02% hydrochloric acid and (2) 0.1 g. of lipase to 0.6 cc. of 0.14% hydrochloric acid. The mixtures were allowed to stand a few minutes, filtered and the hydrogen-ion concentration of the filtrate determined. Mixture 1 had a hydrogen-ion concentration of  $1.8 \times 10^{-5}$ ;

<sup>9</sup> Clark and Lubs, *J. Bact.*, 2, 1 (1917).

# CASTOR BEAN LIPASE.

Mixture 2,  $0.9 \times 10^{-5}$ . The optimum acidity for castor bean lipase activity, therefore, is close to  $C_{H+} 1 \times 10^{-5}$ . This is about the same as that found for gastric lipase by Davidsohn,<sup>10</sup> viz.,  $10^{-4}$  to  $10^{-5}$ . When organic acids, that ionize comparatively little, are used less care need be taken to adjusting the amount of acid to the enzyme. Both acetic and lactic acids can be used with good results over a fairly wide range of percentage concentration.

## The Action of Castor Bean Lipase on Hard Fats.

Fats with high melting points, obviously, do not form emulsions with lipase material and water; hence it is not surprising that they show a low rate of hydrolysis. In order to overcome this difficulty we introduced various fat solvents into the digestion mixtures in the hope of getting better physical contact between enzyme and substrate and thus accelerating hydrolysis. Paraffine oil and ethyl ether were unsatisfactory, comparatively little digestion occurring when either was present. Petroleum ether can be added to advantage in the hydrolysis of an oil by lipase and with marked effect in the hydrolysis of a hard fat. Table VI shows the results obtained with and without petroleum ether.

TABLE VI.

EFFECT OF PETROLEUM ETHER ON THE HYDROLYSIS OF FATS BY CASTOR BEAN LIPASE. The proportions used in each digestion were 0.1 g. of lipase powder, 0.2 g. of fat and 0.6 cc. of 0.1 *N* acetic acid. One cc. of petroleum ether was added to the mixtures containing ether.

Duration of Experiment. Hours.	Olive Oil.		Tallow.	
	Cc. of 0.1 <i>N</i> NaOH. Without ether.	With ether.	Cc. of 0.1 <i>N</i> NaOH. Without ether.	With ether.
24	5.1	5.8	0.2	6.5
48	5.8	5.8	0.2	6.6
72	5.8	5.8	0.2	6.6

## Summary.

A satisfactory method of preparing lipase material from castor beans is to extract the crushed, hull-free kernels with petroleum ether.

The lipase zymogen of castor beans appears to be somewhat soluble in fats or in a mixture of fat and ethyl ether. It is insoluble in ethyl ether in the absence of fats.

Lipase zymogen is activated by acid. The active enzyme is unstable and rapidly destroyed in an acid medium in the absence of fats. In the presence of fats the enzyme shows much greater stability.

The optimum hydrogen-ion concentration for castor bean lipase activity is about  $1 \times 10^{-5}$ . As acidity increases above this point lipolytic activity falls off. At a hydrogen-ion concentration of about  $1 \times 10^{-3}$  activity stops entirely.

<sup>10</sup> Davidsohn, *Biochem. Z.*, 49, 249 (1913).

Petroleum ether added to a mixture of a hard fat, acid, water and castor bean lipase accelerates hydrolysis to a great extent. The hydrolysis of oils is similarly somewhat hastened.

COLUMBUS, OHIO.

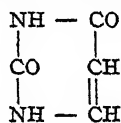
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY.]

## RESEARCHES ON PYRIMIDINES. XCII. NEW METHODS OF IDENTIFYING THE PYRIMIDINE, THYMINE.

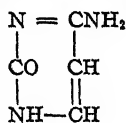
BY TREAT B. JOHNSON AND OSKAR BAUDISCH.

Received August 29, 1921.

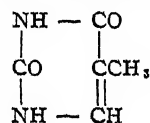
Of the three pyrimidines which have so far been found as products of hydrolysis of nucleic acids only two, namely, uracil (I) and cytosine (II), can be identified by means of characteristic color reactions. Wheeler and Johnson<sup>1</sup> developed a delicate test for these two pyrimidines which



(I).



(II).



(III).

is applied by first oxidizing them in aqueous solution with bromine and then treating the resulting solution with an excess of barium hydroxide. A characteristic purple color develops under such conditions, due to the formation of the barium salt of dialuric acid, which permits of the identification of these two pyrimidines when present in very small quantities. Thymine (III) or any pyrimidine of this type containing alkyl groups in Positions 4 or 5 of the pyrimidine ring fails to respond to this characteristic test.

On account of the important rôle which thymine plays in the chemical processes operating during the growth and destruction of the living cell, it is very important to have available also a characteristic color reaction for the detection of this pyrimidine. A color test which would permit the identification of thymine in the presence of uracil, cytosine and sugar would be of the greatest value in any investigation dealing with the constitution of nucleic acids. The basic properties of cytosine permit its separation from uracil and thymine, but up to the present time we have had no method of identifying small quantities of thymine in the presence of uracil and sugars.

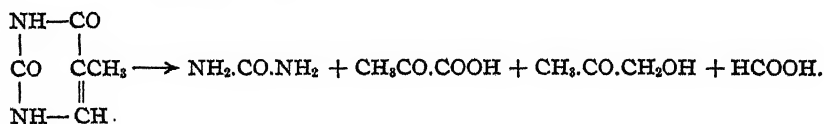
We are able to announce in this paper the discovery of color reactions which are as characteristic for thymine as the dialuric acid reaction is for the identification of the pyrimidine uracil. We find that the thymine molecule is completely destroyed at ordinary temperature, when subjected

<sup>1</sup> Wheeler and Johnson, *J. Biol. Chem.*, 3, 183 (1907).

in aqueous solution to the oxidizing and reducing action of the system, ferrous sulfate plus sodium hydrogen carbonate plus air,<sup>2</sup> with cleavage of the pyrimidine ring and formation of pyruvic acid, acetol, urea and formic acid. The urea is easily identified by the properties and melting point of its characteristic grouping with xanthydrol,<sup>3</sup> while the formic acid is recognized by its reducing action on silver salts.

For the detection of the two remaining products of oxidation namely, pyruvic acid and acetol, we have made use of reactions already described in the chemical literature, and it is on two specific reactions that we base our color tests, which we now bring forward as an indirect proof of the presence of thymine. The identification of pyruvic acid as a product of oxidation of thymine is shown conclusively by its behavior towards *o*-nitro-benzaldehyde in alkaline solution when, as is well known, they interact to form the dye indigo.<sup>4</sup> The color reaction of pyruvic acid with sodium nitroprusside cannot be utilized in our work as a direct test for this reagent on account of the presence of urea, which we find interacts also with the nitroprusside giving a similar highly colored solution. For the detection of acetol we utilize the very susceptible and specific reaction first developed by Baudisch,<sup>5</sup> who has shown that this ketone alcohol interacts smoothly in alkaline solution with *o*-amino-benzaldehyde with formation of 3-oxyquinaldine. Both of these reactions are extremely sensitive and applicable in very great dilution.

These reactions, which are applicable for the detection of these two aliphatic combinations resulting by oxidation of thymine, serve, therefore, for the indirect identification of this pyrimidine. The discussion of the mechanism of the change whereby thymine undergoes destructive oxidation is reserved for a future paper. At present we may represent this transformation as follows.



The discovery that the pyrimidine ring in such combinations as uracil, cytosine and thymine may be destroyed by oxidation at such low temperature in the presence of iron salts, and the identification of pyruvic acid and acetol as normal products of oxidation of thymine are new facts of the greatest biochemical interest in that they reveal possible fundamental chemical changes which the pyrimidine ring actually undergoes in the normal metabolic transformations of the cell.

<sup>2</sup> Baudisch, *Ber.*, 54, 406 (1921).

<sup>3</sup> R. Fosse, *Compt. rend.*, 145, 813 (1907); *Ann. inst. Pasteur*, 30, 525, 673 (1916).

<sup>4</sup> Baeyer, *Ber.*, 15, 2856 (1882).

<sup>5</sup> Baudisch, *Biochem. Z.*, 89, 279 (1918).

### Experimental Part.

While it has been shown that the oxidation of uracil, cytosine and thymine leads to products of physiological interest, a description of these experiments and the discussion of the theory of these oxidations will be deferred for publication in a later paper. At this time we shall confine ourselves to the practical method of applying our new color reactions for the detection of thymine in the presence of other pyrimidines.

A description of a single experiment will suffice to reveal the interesting behavior of thymine when subjected to the oxidizing action of the system, ferrous sulfate plus sodium hydrogen carbonate plus air. Two and six-tenths g. of recrystallized thymine was dissolved in about 100 cc. of hot water and this solution then poured into one of 200 g. of sodium hydrogen carbonate dissolved in 2 liters of water. A 5-liter flask serves best for this operation. To this solution of thymine and bicarbonate is then added 100 g. of crystallized ferrous sulfate dissolved in 500 cc. of water, and the resulting mixture then agitated violently. Colorless iron hydrogen carbonate precipitates at once and will remain in this condition if protected from the air. On agitation of the solution, however, with exposure to the air this carbonate precipitate gradually assumes a green color, due to the absorption of oxygen from the air, with formation of an unstable peroxide. One proceeds to agitate the mixture thoroughly when the oxidation of the thymine takes place immediately and the greenish-gray color of the carbonate precipitate disappears slowly and the carbonate finally assumes a brownish color and the appearance of iron hydroxide. This oxidation and change in the carbonate take about  $\frac{3}{4}$  hour. The mixture is now poured into a filtering jar and allowed to stand overnight when a clear colorless solution is obtained and the iron hydroxide deposits as a dense layer on the bottom of the jar. This clear solution is not characterized by any special odor and is colorless.

The final change in the process of oxidation is brought about by transferring the supernatant liquid to a large evaporating dish and heating the solution on a steam-bath. Hydrolysis takes place under these conditions and the solution acquires an odor characteristic of an alkaline sugar solution when heated. After heating long enough to bring about the above change, 100 to 200 cc. of the clear solution is evaporated to dryness; the residue dissolved again in distilled water and the evaporation repeated. Pyruvic acid is not volatile with steam while acetol vaporizes easily. The dry residue is then dissolved in a small volume of water and the indigo test for pyruvic acid applied as follows: to 5 to 10 cc. of the cold solution are added a few drops of *o*-nitro-benzaldehyde, and the mixture is shaken with chloroform after the addition of 1 to 2 cc. of conc. potassium hydroxide solution. On shaking, the indigo forms immediately and dissolves in the chloroform giving a characteristic blue solution. The formation of indigo



is hastened by warming the solution to be tested and agitating this with the nitro-benzaldehyde until an emulsion is formed and then shaking with chloroform and alkali. Under these conditions a deep blue chloroform solution is obtained and the reaction is so delicate that this characteristic blue color can be obtained easily with solutions representing as low as 2 to 5 mg. of thymine.

In order to apply successfully the test for acetol the remainder of the original thymine solution is subjected to distillation by boiling over a free flame. The distillate at first possesses no reducing properties and is odorless, but as the distillation is continued the characteristic sugar smell develops and finally the distillate acquires the property of reducing Fehling's solution and also ammoniacal silver solution. In order to test for acetol the total distillate is combined with a few drops of *o*-amino-benzaldehyde, potassium hydroxide solution is added until the mixture is distinctly alkaline, and the solution is finally boiled for a few minutes in a beaker. After cooling, the solution is acidified directly with dil. hydrochloric acid, and then made it alkaline again with sodium hydrogen carbonate solution when a characteristic blue fluorescence develops as a result of the formation of 3-oxyquinaldine. For a more exact determination of the acetol the sodium hydrogen carbonate solution is extracted with ether, the ether solution carefully dried and finally distilled when nearly colorless needles are obtained, which have the correct melting point and possess the characteristic properties of 3-oxyquinaldine. An alcoholic solution of the quinaldine develops after dilution with water a deep blue fluorescence, and on adding an alcoholic solution of iron chloride the characteristic deep red complex iron salt of 3-oxyquinaldine is obtained. This red salt is destroyed immediately by addition of acid.

The formation of 3-oxyquinaldine from acetol and *o*-amino-benzaldehyde is a reaction which was first discovered by Baudisch<sup>5</sup> and is one which is specific for this ketone alcohol. The formation of the quinaldine in the distillate of the oxidized thymine proves the formation of acetol as a product of oxidation of this pyrimidine, which is a discovery of the greatest biochemical interest.

Uracil behaves in an entirely different manner from thymine towards the system ferrous sulfate plus sodium hydrogen carbonate plus air. Both pyrimidines are oxidized apparently in a similar manner, but uracil cannot lead to the production of pyruvic acid on account of the absence of a methyl group in Position 5 of the pyrimidine ring. Consequently according to our procedure uracil and thymine can be tested for in the presence of each other, which has not been possible hitherto.<sup>6</sup> In fact, we have been able to demonstrate that it is possible to detect thymine easily in the presence of uracil and cytosine by application of our method. Mixtures of 0.5 g.

<sup>5</sup> See *J. Biol. Chem.*, **4**, 407 (1908).

each of uracil and cytosine and also of uracil and cytosine with small quantities of thymine (0.15 g.) were oxidized according to the procedure described above, and the test for thymine applied. In no case were we able to obtain the characteristic blue color reactions except in those mixtures into which thymine had been introduced.

In this paper we have recorded only the qualitative characteristics of our colorimetric test for the pyrimidine, *thymine*. When the pyrimidine has been prepared in quantity and, therefore, sufficient material is available for research this oxidation reaction will be investigated more carefully and from a quantitative point of view.

Our work to date shows that the system, ferrous sulfate plus sodium hydrogen carbonate plus air, is characterized by its specific oxidizing and reducing action, which may be utilized for bringing about fundamental changes in organic combinations of biochemical interest. The writers are now engaged in the study of several of these transformations and will extend the investigation to new fields of research in which it is anticipated that the ferrous hydroxide-peroxide reagent will reveal still further new transformations of biochemical interest.<sup>7</sup>

### Summary.

1. It has been shown that ferrous hydroxide-peroxide is a sufficiently strong oxidizing agent to destroy the pyrimidine ring at a very low temperature.

2. Uracil, thymine and cytosine are completely destroyed by interaction with this reagent leading to the formation of products which are easily hydrolyzed to urea and aliphatic combinations.

3. In the case of thymine it has been definitely established that pyruvic acid and acetol are normal products of oxidation. These compounds can be identified easily by characteristic color reactions, which serve indirectly as reliable tests for thymine.

NEW HAVEN, CONNECTICUT.

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<sup>7</sup> Our methods of testing for uracil, cytosine and thymine will find immediate practical application in the study of constitution of nucleic acids, and in the research on *tubercle bacillus* now in progress in this laboratory (T. B. Johnson).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

# THE C<sub>4</sub>-SACCHARINIC ACIDS. II. THE PREPARATION AND RESOLUTION OF dl-1,3-DIHYDROXY-BUTYRIC ACID. SOME DERIVATIVES OF THE OPTICALLY-ACTIVE ACIDS.

By J. W. E. GLATTFELD AND FRANK V. SANDER.<sup>1</sup>

Received August 29, 1921.

The first two C<sub>4</sub>-saccharinic acids to be prepared in this laboratory and studied in detail, were the two optically-active 2,3-dihydroxy-butyric acids.<sup>2</sup> The present paper is a report of the results of a similar study of the optically-active 1,3-dihydroxy-butyric acids. The object of this work is to provide material with which to study the properties of the saccharinic acids, to find means of identifying the individual acids, and to devise methods for separating them from each other in such mixtures as are obtained when sugars are treated with alkalies.

The acid under consideration has been obtained in its inactive form by Nef<sup>3</sup> and his students in the course of their work on the effect of alkalies on the various sugars. Nef not only obtained the *dl*-acid but resolved it into the active components and proved the configuration of the *d*-acid



to be CH<sub>2</sub>.OH.C.C.-COOH by oxidation to *d*-malic acid. He also gives



some information as to constants of the brucine salt, phenylhydrazide and lactone of the *dl*-acid, as well as the brucine salt, quinine salt and lactone of the *d*-acid and the brucine salt of the *l*-acid. His study of the *l*-acid was apparently very superficial.

The *dl*-acid and the *dl*-calcium salt have been prepared also by Raske<sup>4</sup> in the course of his investigation of the action of cyanides on chlorinated aldehydes. He obtained from 2-chloro-propionaldehyde and cyanides, 1-oxy-3-chloro-butyric acid which was converted into 1,3-dihydroxy-butyric acid when boiled with water.

The above is a summary of all the work that has been published on the acid under consideration. Neither of the methods by which the acid had been prepared was considered suitable for the object of the work below. It was therefore prepared, by a method similar to Raske's, from 2-hydroxy-propionaldehyde by the addition of hydrogen cyanide and subsequent

<sup>1</sup> The dissertation of which this paper is a condensation was presented by Frank V. Sander as part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago. The original dissertation is on file in the University of Chicago Library.

<sup>2</sup> Glatfeld and Miller, *THIS JOURNAL*, **42**, 2314 (1920).

<sup>3</sup> Nef, *Ann.*, **376**, 1-120 (1910). Upson, *Am. Chem. J.*, **45**, 458 (1911).

<sup>4</sup> Raske, *Ber.*, **45**, 725 (1912).

hydrolysis of the nitrile. In the course of this study, Nef's entire work on this acid was repeated and the study of the *l*-acid completed.

### Experimental Part.

The starting material for the synthesis was acrolein which had been prepared from dry glycerin and anhydrous magnesium sulfate, according to the method of Witzemann.<sup>5</sup> The crude acrolein was introduced into a steel cylinder with 4 volumes of water<sup>6</sup> and heated in a boiling water-bath for 20 hours. The solution was then subjected to complete distillation at 60° and 14 mm. in one operation by siphoning liquid into the distilling flask as fast as water distilled. The gummy residue was then distilled from an oil-bath at a low temperature and pressure. It was found that a much higher yield could be obtained when the total quantity of gummy residue was subjected to distillation in one operation than if divided into 4 portions, as suggested by Nef, and each portion subjected to distillation separately. The best results were obtained when the temperature of the oil-bath was kept about 10° above that of the vapor in the flask, and it was only by very slow and careful distillation that maximum yields could be obtained from the crude aldehyde. The yield of redistilled aldehyde of boiling range 80–86° at 14 mm. from 400 cc. of crude acrolein, averaged 95 g. The pure aldehyde can be redistilled with practically no decomposition and may be considered a fairly stable substance.

The pure aldehyde dissolved in water was treated with hydrogen cyanide, etc., in the usual manner. The hydrolysis of the nitrile was effected with conc. hydrochloric acid. The black gum which remained after subjecting the reaction mixture to complete distillation was extracted with boiling ethyl acetate and with hot ether. The acid recovered from these solutions was again extracted with hot ether. The average yield of the clear, yellow, mobile acid recovered from the ether was about 70% of the amount calculated from the pure aldehyde. The crude acid was converted into the calcium salt by means of calcium carbonate, and trituration with alcohol, etc. From 92 g. of crude acid there was obtained an average yield of 92 g. of dry powdery salt.

*Pure dl-Acid.*—The acid gum obtained from the calcium salt by means of oxalic acid, etc., was first dried as completely as possible in a boiling water-bath at 14 mm. A glycerine-bath was then substituted for the water-bath and the water pump was replaced by an oil pump. A perfectly clear, mobile, and in some cases odorless, liquid distilled over, boiling point at 4 mm. 104°, and at 3 mm. 102°. The distillate was titrated with 0.1 *N* sodium hydroxide with the following results.

<sup>5</sup> Witzemann, *THIS JOURNAL*, 36, 1766 (1914).

<sup>6</sup> Nef, *Ann.*, 335, 219 (1904).

	Sample. G.	0.1 N NaOH. For free acid. <sup>7</sup> Cc.	Total required. Cc.	Calc. for C <sub>4</sub> saccha- rinic, acid lactone. Cc.
I	0.2462	0.05	24.18	24.14
II	0.2832	0.05	27.90	27.77

It is evident that the liquid was practically pure lactone. It is soluble in about 12 parts of warm ether.

Five g. of the lactone, with phenyl hydrazine, etc., gave 8.53 g. of crystals, m. p. 130°. The melting point was unchanged when the substance was recrystallized. As Nef reports a melting point of 130° for his *dl*-hydrazide from *l*-arabinose, these two substances were evidently identical.

**The Resolution of the *dl*-1,3-Dihydroxy-butyric Acid.**—To 36 g. of the acid lactone which had a boiling point of 102° at 3 mm., was added, in one liter of water, 165 g. of brucine. After the usual procedure<sup>8</sup> 182 g. of crude brucine salts was obtained. A sample of this crude salt after a treatment with benzene to remove any free brucine and drying to constant weight over sulfuric acid *in vacuo*, was found to have a specific rotation of -26.73°, *i. e.*, 1 g. in 24 g. of water at approximately 20° gave  $\alpha = -2.16^\circ$  in a 2 dcm. tube; sp. gr. 1.010.

The *dl*-brucine salt was now dissolved in twice its weight of hot water. The solution was allowed to stand overnight during which time crystals were deposited (Crop I from water, see below) which were removed by filtration. The filtrate was concentrated until the ratio of water to salt was again 2:1. This solution again yielded a crop of crystals. When no more crystals could be obtained in this way from water, the solution was subjected to complete distillation at 60° and 14 mm. and the residue dissolved in 10 parts of boiling absolute alcohol. When the solution had cooled, the crystals deposited (Crop I from alcohol, see below) were removed by filtration, and the filtrate concentrated until the ratio of salt to alcohol again was 1:10. This process was continued until no more crystals could be obtained. The following table shows the results. The crystals were dried to constant weight *in vacuo* over sulfuric acid, and in each case a 1g. sample was dissolved in 24 g. of water. The specific gravity was found to be 1.010 and readings were taken in a 2dcm tube at approximately 20°.

Crops I, II and III from water were united and recrystallized from 2 parts of water. This process gave 65 g. of crystals. The specific rotation was -20.79. Six subsequent recrystallizations from 2 parts of water gave crops each of which had a specific rotation of -20.79°. This indicates that the substance was the pure brucine salt of one of the optical components of the *dl*-acid. The melting point of this brucine salt was 169°.

<sup>7</sup> Ref. 2, p. 2317, footnote.

<sup>8</sup> Glatfeld and Hanke, *THIS JOURNAL*, 40, 976 (1918), footnote.

FROM WATER.	Parts of water used.	Weight. G.	$\alpha$ . Observed.	$[\alpha]_D^{20}$ .
I	2	49	$-1.68^\circ$	$-20.79^\circ$
II	2	8	$-1.71^\circ$	$-21.16^\circ$
III	1	20	$-1.72^\circ$	$-21.28^\circ$
Residue		104		
FROM ABSOLUTE ALCOHOL.	Parts of alcohol used.	Weight. G.	$\alpha$ . Observed.	$[\alpha]_D^{20}$ .
I	10	75	$-2.77^\circ$	$-34.28^\circ$
II	10	18	$-3.09^\circ$	$-38.23^\circ$
III	10	1	$-3.18^\circ$	$-39.35^\circ$
Residue		9.2		

Crops I, II and III from alcohol were united and recrystallized from 10 parts of alcohol, and thus 78 g. of crystals was obtained with a specific rotation of  $-32.67^\circ$ . Six subsequent recrystallizations from 10 parts of absolute alcohol gave crops each of which had a specific rotation of  $-32.67^\circ$ . This indicates that the substance was the pure brucine salt of the other optical component of the *dl*-acid. The melting point of this acid was  $169^\circ$ .

In all cases of recrystallization from alcohol, the mother liquors when concentrated *in vacuo* at  $60^\circ$  yielded second crops of crystals, the specific rotations of which were much higher than  $-32.67^\circ$ , the invariable rotation of the first crops. That this was due to free brucine was shown as follows. When separate samples from Crops I, II and III, from alcohol,  $[\alpha]_D^{20}$   $-34.28$ ,  $-38.23$ ,  $-39.35$ , respectively, were refluxed for 2 hours with benzene, the specific rotations of the extracted brucine salts fell in each case to  $-32.67^\circ$  and the benzene was shown to contain brucines. Hydrolysis was not observed in the case of recrystallization of the pure brucine salt of low rotation from water. This salt is apparently perfectly stable in water solution. Furthermore the specific rotation of this salt was not changed after it had been boiled for 2 hours with benzene under a reflux condenser.

**The Optically-active 1,3-Dihydroxy-butyric Acids.**—The active acids were obtained by the usual method<sup>9</sup> from the pure brucine salts by treatment with barium hydroxide, etc. The crude acid was distilled at 3 mm. and the distillate in each case was a perfectly colorless, transparent, mobile, odorless liquid with a boiling point of  $96^\circ$ . The yield from 100 g. of brucine salt  $[\alpha]_D^{20} -20.79^\circ$ , was 18.0 g. and from 100 g. of brucine salt  $[\alpha]_D^{20} -32.67^\circ$ , was 17.8 g.

The specific rotations of the two acids were now determined with the following results. In each case an exactly 4% solution was used in a 2dm. tube. The specific gravity was 1.010 and observations were made at approximately  $20^\circ$ .

The figures show that equilibrium between free acid and lactone was reached in water solution at ordinary temperatures in 7 days. Experi-

<sup>9</sup> Ref. 8, p. 981, footnote.

	$\alpha$ . Obs. 5 min.	$\alpha$ . Obs. 7 days.	$\alpha$ . Obs. 12 days.	$[\alpha]_D^{20}$ . 5 min.	$[\alpha]_D^{20}$ . 7 days.	$[\alpha]_D^{20}$ . 12 days.
Acid from $-20.79^\circ$ brucine salt.....	+1.64°	+1.21°	+1.21°	+20.29°	+14.97°	+14.97°
Acid from $-32.67^\circ$ brucine salt.....	-1.62°	-1.20°	-1.20°	-20.05°	-14.86°	-14.86°

ments with these acids showed that equilibrium was reached at  $100^\circ$  in water solution in 4 hours.

Samples of the two acids were titrated with the following results.

		0.1 N NaOH.		
	Sample G.	For free acid. Cc.	Total re-quired. Cc.	Calculated for C <sub>6</sub> -saccharinic acid. Cc.
Acid from $-20.79^\circ$ brucine salt I.....	0.3759	0.05	36.87	36.85
II.....	0.2531	0.10	24.74	24.81
Acid from $-32.67^\circ$ brucine salt I.....	0.3117	0.05	30.48	30.56
II.....	0.2001	0.05	19.48	19.62

The above results show that the acids were practically entirely in the form of lactone.

**Proof of Configuration of the Optically-active Acids.**—Although Nef<sup>10</sup> had already proved the configuration of the acid of positive rotation, which he obtained from *l*-arbinose, by oxidizing it to *d*-malic acid, his work was repeated and the acid of negative rotation also oxidized. The procedure outlined by Glattfeld and Miller in the first paper,<sup>2</sup> was followed. In each case 5 g. of the optically-active acid was oxidized, and the experimental data thus obtained are tabulated below. An exactly 4% solution was observed in a 2cm. tube at approximately  $20^\circ$ . The specific gravity was determined as 1.010.

Oxidation of acid.	Insoluble calcium salt obt. G.	Cryst. acid obt. from calcium salt. G.	$\alpha$ . Observed of crystallized acid.	$[\alpha]_D^{20}$ of crystallized acid.	M. p. of cryst. acid. ° C.
1. Positive rotation.....	3.42	2.37	+ .27°	+3.34°	101
2. Negative rotation.....	3.24	2.17	- .26°	-3.22°	101

The following results were obtained by titration of the 2 crystalline acids obtained as oxidation products of the 2 dihydroxy acids.

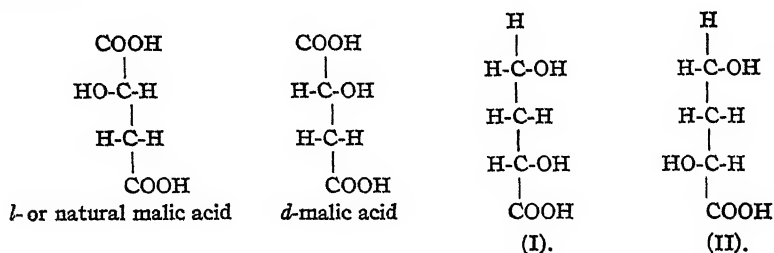
	Sample G.	0.2 N NaOH. Used. Cc.	Calculated for malic acid. Cc.
+3.34° acid I.....	0.5106	38.21	38.11
II.....	0.4987	37.10	37.18
-3.22° acid I.....	0.3061	22.90	22.84
II.....	0.3893	29.21	29.05

When natural or *l*-malic acid was purified in the same way as the acid obtained above by the oxidation of the dihydroxy-butyric acid of negative

<sup>10</sup> Nef, *Ann.*, 376, 36 (1910).

rotation, it was found to have a specific rotation of  $-3.34^\circ$  and a melting point of  $101^\circ$ . These constants are practically the same as those of the crystalline acid from the oxidation of the dihydroxy-butyric acid of negative rotation. That the two acids were identical was finally shown by a mixed-melting-point determination. A mixture of the 2 acids melted at  $101^\circ$ .

The above facts show that the acid having  $[\alpha]_D^{20} - 14.86^\circ$  gives natural or *l*-malic acid which has the following configuration, as was shown by Fischer.<sup>11</sup>



Of the two 1,3-dihydroxy-butyric acids only the one with the configuration I (above) can give *l*-malic acid. This must then be the configuration of the dihydroxy-butyric acid  $[\alpha]_D^{20} - 14.86^\circ$  and it must be called *l*-1,3-dihydroxy-butyric acid. In the same way Configuration II (above) must be the configuration of the acid  $[\alpha]_D^{20} + 14.97$  since it gives by oxidation *d*-malic acid, and it must be called *d*-1,3-dihydroxy-butyric acid

### Some Derivatives of the Active Acids.

*The Strychnine Salts.*—The strychnine salts were obtained as well defined crystals from alcohol, but seemed to be hydrolyzed quickly by water.

*The Quinine Salts.*—The quinine salts were made from the pure *d*- and *l*-acids in the usual manner except that the solutions were extracted with chloroform instead of benzene to remove free quinine. The quinine salt of the *d*-acid crystallized from 2 parts of absolute alcohol and the salt of the *l*-acid from 4 parts of absolute alcohol. Thus the solubilities of these 2 salts are the reverse of those of the brucine salts, a fact which may be of value in some cases of separation. The following constants were determined.

	Quinine salt.	$\alpha$ . Observed.	$[\alpha]_D^{20}$ .	M. p. ° C.
(a)	<i>d</i> -acid	$-4.30^\circ$	$-106.4^\circ$	149
(b)	<i>l</i> -acid	$-9.93^\circ$	$-122.9^\circ$	149

(a) 0.3000 g. present in 7.5 g. of water. The angle of rotation was observed in a 1dcm. tube at approximately  $20^\circ$ ; sp. gr. taken as 1.010.

(b) 1.000 g. present in 25.00 g. of water. The angle of rotation was observed in a 2dcm. tube at approximately  $20^\circ$ ; sp. gr. taken as 1.010.

*The Calcium Salts.*—The calcium salts of the pure *d*- and *l*-acids were

<sup>11</sup> Fischer, *Ber.*, 29, 1378 (1896).



made. After treatment with excess calcium carbonate, filtration, and complete distillation of the clear filtrate *in vacuo*, a solid porous white mass was obtained, whereas with the *dl*-acid a clear yellow gum was obtained at this point. The crude salts were recrystallized from water. When 2 parts of water were used a moist pliable mass of interwoven needle-like crystals was obtained, while in 3 parts of water very few crystals were formed.

From 5 g. of *d*-1,3-dihydroxy-butyric acid, there was obtained from water 5.57 g. of a beautifully crystalline salt which after several recrystallizations from 2 parts of water gave a constant specific rotation of  $+17.08^\circ$ , *i. e.*, an exactly 4% aqueous solution in a 1dcm. tube at approximately  $20^\circ$  gave  $\alpha + 0.69^\circ$ ; sp. gr. taken as 1.010. This salt decomposes when heated at  $220$ – $225^\circ$ .

The calcium salt of the *l*-acid was made in exactly the same way as that of the *d*-acid. This salt was made twice from the lactones of  $[\alpha]_D^{20} -20.91^\circ$  and  $-20.05$ , the rotation of each lactone being taken after 5 minutes in solution. The first crops from 2.5 parts of water had specific rotations of  $-8.66^\circ$  and  $-3.80$ . Evidently these crops were not the normal salts of the acid.<sup>12</sup> The filtrates from these first crops of crystals were concentrated and the residues dried completely at  $100^\circ$  and 14 mm. The gummy residues were then made crystalline by trituration with absolute alcohol. The salts so obtained were apparently the normal salts of the acid as was shown by their specific rotations  $-17.33^\circ$  and  $-17.01^\circ$ , respectively.

An analysis of the calcium salts of the *d*- and *l*-acids was made. The salts were ignited to constant weight in a platinum crucible with the following results.

Calcium salt. Rotation.	Sample. G.	Constant wt. dried at $100^\circ$ . G.	Loss of water %.	Constant wt. of ash. G.	CaO. %.
$+17.08^\circ$	0.3503	0.3103	11.42	0.0627	17.89
$-17.33^\circ$	0.3169	0.2806	11.45	0.0568	17.92
Calc. for $\text{Ca}(\text{C}_4\text{H}_7\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$			11.46		17.83

The cinchonine and barium salts and the phenylhydrazides of the two pure acids were made but all proved to be gums.

### Summary.

*dl*-1,3-Dihydroxy-butyric acid has been prepared from 2-hydroxy-propionaldehyde. The resolution of the *dl*-acid, by means of brucine, into the optical components is reported. Configurations are assigned to the two forms of the acid and proofs of the correctness of these configurations are given. The following constants for the *d*- and *l*-forms of the acid, and some of the derivatives, are given.

<sup>12</sup> The exact nature of these salts has not been determined. A thorough investigation of the calcium salt formation in these cases will be taken up as soon as opportunity offers.

	After 5 min. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> .	At equilibrium. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> .	B. p. at 3 mm. ° C.	Brucine salts. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> .	M. p. ° C.	Quinine salts. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> .	M. p. ° C.	Calcium salts. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> .
<i>d</i> -Acid	+20.29°	+14.97°	96	-20.79°	169	-106.4°	149	+17.08
<i>l</i> -Acid	-20.05°	-14.86°	96	-32.67°	169	-122.9°	149	-17.33

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

## THE PREPARATION OF OPTICALLY-ACTIVE HYDRAZINES.

II. THE PREPARATION OF *dl*-*p*-SECONDARY-BUTYL-PHENYLHYDRAZINE. THE RESOLUTION OF *dl*-*p*-SECONDARY-BUTYL-ANILINE.By J. W. E. GLATTFELD AND EDGAR WERTHEIM.<sup>1</sup>

Received August 29, 1921.

As stated in the first paper<sup>2</sup> of this series these attempts to prepare some optically-active phenylhydrazines have been undertaken in order to supply another set of reagents to supplement the alkaloids in the resolution of such *dl*-hydroxy acids as the saccharinic acids.<sup>3</sup> Furthermore the hope has been entertained that methods of preparation might be found which would make some of the optically-active hydrazines much less expensive than the alkaloids ordinarily used. In the previous attempt only the *dl*-*p*-trimethylethyl-phenylhydrazine was prepared, such attempts as were made to obtain one of the active forms having failed. In the work reported below it was again found impossible in the time at hand to isolate the active forms of the hydrazine prepared (*sec*.-butyl-phenylhydrazine) although the hydrazine was obtained in the *dl* form and the active forms of the corresponding aniline were isolated. In the light of our work up to the present time, it does not seem impossible ultimately to succeed in obtaining some of the active phenylhydrazines and our attempts will therefore continue. In the present paper we report as briefly as seems possible those results of our work that appear to us to be of some general interest or importance.

The plan for the preparation of the optically-active *p*-*sec*.-butyl-phenylhydrazines included first the preparation of *dl*-*sec*.-butyl-aniline, then the resolution of this compound into the two optical isomers, and finally the preparation from these, of the active phenylhydrazines.

In order to prepare *dl*-*p*-*sec*.-butyl-aniline it was necessary first to pre-

<sup>1</sup> The dissertation of which this paper is a condensation was presented by E. Wertheim as part fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago. The original dissertation is on file in the University library.

<sup>2</sup> Glattfeld and Milligan, *THIS JOURNAL*, **42**, 2322 (1920).

<sup>3</sup> Glattfeld and Miller, *ibid.*, **42**, 2314 (1920).

pare and in the order named, the following compounds: (1) "methopropenyl benzene" (1-phenyl-1-methyl-2-methyl-ethylene); (2) *dl-sec.*-butylbenzene; (3) *dl-p*-nitro-*sec.*-butylbenzene. The first two of these compounds are described in the literature,<sup>4</sup> and the methods there set forth have been modified somewhat in the unpublished work of R. J. Williams<sup>5</sup> and A. F. Hardman.<sup>6</sup> The third compound was first prepared by Williams,<sup>5</sup> and his work was repeated and extended by Hardman.<sup>6</sup>

In the present paper the preparation of these three compounds will not be described in detail; only departures from published work and from the ordinary course of synthesis will be noted.<sup>7</sup>

*dl-p-sec.*-Butyl-aniline has recently been prepared by Reilly and Hickinbottom<sup>8</sup> in the course of their investigations in rearrangements of the alkyl-aryl amines. They heated *sec.*-butyl alcohol, aniline and zinc chloride in an autoclave at a high temperature and isolated this compound, as well as other amines, from the reaction mixture. As they prepared and analyzed several derivatives of the compound, their work will be referred to again.

### Experimental Part.

"Methopropenyl benzene" was prepared by the method of Grignard, from acetophenone, ethyl bromide and magnesium turnings. The acetophenone was added to the thoroughly cooled (with ice and salt) and vigorously stirred ether solution of ethylmagnesium bromide and the impure hydrocarbon was obtained by hydrolysis of the reaction product with ice water and, later, dil. sulfuric acid. The product of the reaction consists in large part of methyl-ethyl-phenyl-carbinol. A fact which does not appear to have been noted before is that most of the carbinol can be changed to the olefine by heating to 100° for 20 minutes. Fractions which corresponded to the temperatures *t*-180°, 180-186°, 186-191°, 191-*t*° were taken and dried by means of calcium chloride. Practically the whole of the product after the second fractionation was found in the fraction which had the boiling range 186-191°.

The boiling point of the pure compound is variously reported in the literature. The writer's experience agrees with that of Tiffeneau<sup>4</sup> who gives 186-7° as the boiling point at ordinary pressure. For the purposes of this work the entire fraction 186-191° was used without further treatment for the next step in the synthesis. The best yield of the fraction 186-191° obtained in 12 runs was 82%; the average yield was 73%. These are calculated from the acetophenone used.

For the preparation of *sec.*-butylbenzene, "methopropenyl benzene" was reduced by the use of sodium and moist, but alcohol-free, ether.<sup>5</sup> Freshly cut sodium was dropped through the condenser and into the hydrocarbon which was dissolved in a layer of ether resting upon water. After 75% of the sodium had been introduced, the reduction

<sup>4</sup> Radziszewski, *Ber.*, 9, 260 (1876). Estreicher, *Ber.*, 33, 439 (1900). Klages, *Ber.*, 35, 2641 (1902). Tiffeneau, *Ann. chim. phys.*, [8] 10, 322 (1907).

<sup>5</sup> Williams, M. S. *Thesis* of 1918 on file in University of Chicago Library.

<sup>6</sup> Hardman, M. S. *Thesis* of 1919 on file in University of Chicago Library.

<sup>7</sup> Minute details of the procedure followed throughout this work will be found in the complete dissertation of E. Wertheim on file in the University Library, University of Chicago.

<sup>8</sup> Reilly and Hickinbottom, *J. Chem. Soc.*, 117, 120 (1920).

was interrupted, the ether layer separated from the aqueous layer, and the latter twice extracted with ether and then discarded. The reduction was then resumed as above with a fresh water layer. It was found that removing the alkaline water solution at this stage materially increased the yields. The fraction of boiling range 170–180° was then obtained from the ether layer and extracts and was used for the next step in the synthesis. Most of the liquid distilled at 173–4° which is the boiling point of *sec.*-butyl-benzene given in the literature.<sup>9</sup> The best yield obtained in 11 runs was 77%; the average was 67%.

In preparing the *p*-nitro-*sec.*-butyl-benzene the ordinary course of nitration with nitric and sulfuric acids was followed. The temperature of the reaction mixture was kept between 5° and 10°. The nitro compound was obtained by steam distillation, ether extraction of the distillate, etc. The fraction which had a boiling range of 130–140° at 12 mm. was largely *dl-p*-nitro-*sec.*-butyl-benzene.<sup>10</sup> This fraction was redistilled and the part which boiled at 130° at 9 mm. was pure *dl-p*-nitro-*sec.*-butyl-benzene. The best yield in four runs was 63%; the average was 57%.

The reduction of the nitro compound was carried out in the usual manner with conc. hydrochloric acid and granulated tin. The aniline was obtained from the reaction mixture by the addition of sufficient alkali to make it just alkaline (a large excess of alkali is to be avoided<sup>2</sup>), subsequent distillation with steam, extraction of the distillate with ether, etc. The boiling range of the crude compound was 120–130° at 18 mm. Redistillation yielded pure aniline which boiled at 112° at 11 mm. The boiling point at atmospheric pressure is given by Reilly and Hickinbottom<sup>8</sup> as 238°. The acetyl derivative was prepared by the use of acetyl chloride. It was recrystallized from a mixture of water and 95% alcohol and was found to have a melting point of 125–6°. This is the melting point reported by Reilly and Hickinbottom.<sup>8</sup>

The *dl-p-sec.*-butyl-aniline was analyzed in this laboratory by Mr. Williams.<sup>5</sup> The following results are quoted from his paper.

*Analyses.* Subs., 0.1437, 0.2311: CO<sub>2</sub>, 0.4241, 0.6843; H<sub>2</sub>O, 0.1276, 0.2046. Subs., 0.2938, 0.2994: N<sub>2</sub>, 24.65 cc. (20° and 751 mm.), 24.1 cc. (20° and 749 mm.). Calc. for C<sub>10</sub>H<sub>13</sub>N: C, 80.54; H, 10.07; N, 9.39. Found: C, 80.50, 80.75; H, 9.94, 9.90; N, 9.52, 9.11.

The preparation of *p-sec.*-butyl-aniline was also attempted by the Friedel and Crafts reaction, using acetanilide, *sec.*-butyl chloride, and aluminum chloride. The reaction seemed to go quite smoothly and the desired aniline was obtained by hydrolysis, etc., but in small quantity; the largest yield realized was 14%. The aniline had the proper boiling point, and the acetyl derivative had the proper melting point. When mixed with a sample of the acetyl derivative from the aniline made from acetophenone above, there was no depression of the melting point.

### Resolution of *dl-p-sec.*-Butyl-aniline.

Oxymethylene-camphor and bromo-camphor sulfonic acid were first tried as resolving agents for *dl-p-sec.*-butyl-aniline, but with only partial success. Camphor sulfonic acid was found to be a much better reagent. A typical experiment is described below.

*Levo-p-sec.*-butyl-aniline.—Ten g. of the *dl-p-sec.*-butyl-aniline was placed in a beaker and 10 cc. of 30% acetic acid added. To this mixture was added 17 g. (15.5

<sup>9</sup> Klages, *Ber.*, 35, 3509 (1902).

<sup>10</sup> The position of the nitro group as *para* was established in the work of R. J. Williams to which reference has been made. He oxidized the nitro compound with chromic acid to *p*-nitrobenzoic acid, and proved the identity of the latter substance.

g. required theoretically) of camphor sulfonic acid as a fine powder. The mixture was stirred until the acid had dissolved. This took place readily and with the production of a small amount of heat. The beaker was then kept on an electric hot-plate at 100° for 2 hours, or until a considerable part of the acetic acid had evaporated, and the residue was quite thick.

The mass was then allowed to cool, after which it was broken up with a pestle and twice well-washed by decantation with ice-water. The water which adhered was removed as quickly as possible by the use of a Büchner funnel. The moist compound was pressed between filter papers, and then placed in a vacuum desiccator over sulfuric acid. It was generally quite dry in 5 or 6 days. By this treatment the racemate obtained was fairly pure as shown by the following rotations. These rotations are from 5 different preparations of the racemate.<sup>11</sup>

*Rotations.* Subs., 0.9862, 0.9121, 0.5522, 0.2262, 0.2392.  $[\alpha]_D = +25.98, 25.77, 26.11, 25.97, 26.23$ .

The melting point of the dry racemate was 119–120°; it was a light pinkish-yellow powder, and weighed between 17 and 20 g.

The racemic compound was next treated with 50 to 75 cc. of pure ether, and allowed to stand with frequent stirring for about 2 hours. The supernatant liquid changed in this time to a pink color, and the powder became pure white. The mixture was then subjected to filtration by suction, and the white crystals were washed on the filter with dry ether, and then air-dried. The crystals were recrystallized from a mixture of about 5 parts of ethyl acetate to 1 part of acetone, and then had a melting point of 173–4°. A separation had therefore evidently been effected. The sample at this point usually weighed from 5 to 7 g. Rotations in chloroform showed no change after several crystallizations of the same crop from the solvents named above; the value was invariably near to +32.00. The following figures show the results of one such experiment.<sup>12</sup>

Crop.	Weight. G.	Subs. G.	$[\alpha]_D$
1	6.0	0.2740	+31.95
2	3.8	0.2282	+32.32
3	2.2	0.3038	+31.68
4	0.93	0.2305	+31.62

The following figures for a number of samples show the constancy of the rotation after the first crystallization. These are the rotations of 6 different preparations after the ether treatment of the racemate, and one recrystallization from acetone-ethyl acetate mixture of the crystals insoluble in ether.

*Rotations.* Subs., 0.3329, 0.6062, 0.6050, 0.8351, 0.4915, 0.5539  $[\alpha]_D = +31.47, 31.22, 31.76, 31.43, 31.54, 31.41$ .

From these figures it seems fairly certain that one of the pure components has a specific rotation between +31.5 and 32.00. The free aniline was obtained by treating the camphor sulfonic derivative of this specific rotation first with conc. hydrochloric acid, and treating the crystalline hydrochloride obtained with alkali, etc. The aniline was found to have a light yellow color and to boil at 116.5–118° at 15 mm. pressure. A

<sup>11</sup> All the rotations in this work were made, unless otherwise stated, in chloroform solution, in a 2dcm. tube and at room temperature. The solution was in each case made up to a volume of 25 cc. and quickly filtered, after which the readings were taken with the minimum loss of time.

<sup>12</sup> The 2nd crop (3.8 g.) was obtained by recrystallization of the 1st crop (6.0 g.). The 3rd crop (2.2 g.) was obtained by recrystallization of the 2nd crop (3.8 g.), etc.

sample of this aniline when examined in a 0.5dcm. tube gave  $\alpha = -0.26$ . Analysis of samples gave the following results.

Subs., 0.2986, 0.3022:  $\text{CO}_2$ , 0.8832, 0.8932;  $\text{H}_2\text{O}$ , 0.2724, 0.2796. Subs., 0.3386, 0.3422:  $\text{N}_2$ , 29.4 cc. ( $24^\circ$  and 740.5 mm.), 29.5 cc. ( $24.5^\circ$  and 748 mm.). Calc. for  $\text{C}_{10}\text{H}_{13}\text{N}$ : C, 80.54; H, 10.07; N, 9.39. Found: C, 80.67, 80.61; H, 10.14, 10.23; N, 9.49, 9.46.

The acetyl derivative was made by treating the aniline with acetyl chloride, and the resulting crystals were recrystallized from a mixture of water and 95% alcohol. The pure white crystals were found to have a melting point of  $123-4^\circ$ . When the rotation of a sample of 0.5376 g. was taken in chloroform solution, the specific rotation was found to be  $[\alpha]_D^{25} = +0.9301$ .

**Dextro-*p*-sec-Butyl-aniline.**—The dextro-rotatory aniline was obtained from the soluble camphor sulfonic acid derivative left in the filtrates after the crystalline derivative had been removed (see above). This soluble compound remained as a dark-brown or black semi-solid gum after all of the solvent had been removed by evaporation. Solutions were too dark for determination of the rotation.

The gum was first dissolved in sodium-dried ether and separated by filtration from a few crystals of the less soluble isomer which it contained. The ether was next removed by evaporation, and the gum covered with conc. hydrochloric acid and heated to  $100^\circ$  for 5 hours. Excess of sodium hydroxide was then added, and the aniline recovered as usual. The boiling point of the aniline was  $123-5^\circ$  at 20 mm. Part of this sample was placed in a 0.5dcm. tube and gave  $\alpha = +0.26$ . This rotation is equal and opposite to that of the aniline from the crystalline camphor sulfonic compound, and indicates that the sample was probably pure.

An attempt to convert 9.6 g. of the *l*-sec-butyl-aniline into the active phenylhydrazine failed entirely although the procedure under which the *dl*-aniline had been successfully converted into the *dl*-hydrazine (see below) was followed carefully. Furthermore, these conditions failed also in one instance in the making of the *dl*-hydrazine. No reason for these failures can be offered at the present time, but it is hoped that perfect conditions for the conversion will ultimately be found.

### Preparation of *dl*-*p*-sec-Butyl-phenylhydrazine.

This compound was prepared from the corresponding aniline as follows.

The aniline was first treated with conc. hydrochloric acid and diazotized. The addition of the nitrite solution took some time as it was found to be important to keep the temperature of the reaction mixture always below  $0^\circ$ . The diazonium salt solution was poured at once into a cold solution of sodium sulfite, giving a rich red solution, a sample of which was only slightly cloudy after having been boiled for one minute. This solution was then reduced in the usual way by the Fischer method<sup>13</sup> with zinc dust and acetic acid. The reaction mixture was heated nearly to the boiling point during the reduction in order to make sure of completeness of reduction. From the cooled solution the solid sulfonate was separated by filtration.

The *dl*-*p*-sec-butyl-phenylhydrazine sodium sulfonate crystallizes from a water solution in beautiful white plates with a pearly lustre. These are stable in the air for about 2 hours when they darken slightly. After one crystallization from 95% alcohol the crystals were well dried in a vacuum desiccator over sulfuric acid.

<sup>13</sup> Fischer, *Ann.*, 190, 67 (1877).

*Analyses.* Subs., 0.1743, 0.1626: N<sub>2</sub>, 15.4 cc. (19° and 753.4 mm.), 14.8 cc. (21.3° and 754.8 mm.).

Subs., 1.0948, 1.3103: BaSO<sub>4</sub>, 0.9557, 1.1544. Calc. for C<sub>10</sub>H<sub>15</sub>N<sub>2</sub>SO<sub>3</sub>Na: N, 10.53; S, 12.03. Found: N, 10.11, 10.36; S, 11.99, 12.10.

To obtain the hydrochloride of the hydrazine, the sulfonate was covered with conc. hydrochloric acid, and the mixture heated to boiling for 8 hours, during which time fresh acid was supplied as needed. The solid hydrochloride was obtained as a mass of white crystals from the cooled solution. These were treated with sodium hydroxide, etc., to give the hydrazine. The crude hydrazine was subjected to distillation at reduced pressure in an atmosphere of hydrogen and boiled at 145–158° at 16 mm. When redistilled it had a boiling range of 155–7° at 18 mm.

The *dl-p-sec.*-butyl-phenylhydrazine is a thick light-yellow oil when first distilled but soon turns to a maroon color in the air. In sealed tubes it keeps its light yellow color indefinitely.

*Analyses.* Subs., 0.2390, 0.2023: N<sub>2</sub>, 36.5 cc. (22.0° and 738.5 mm.), 31.4 cc. (25.8° and 745 mm.).

Calc. for C<sub>10</sub>H<sub>15</sub>N<sub>2</sub>: N, 17.03. Found: 16.85, 16.99.

Only a small amount of the *dl*-hydrazine was available for a study of derivatives and consequently only a few preliminary tests could be made. It seems to form only gummy derivatives with *d*-glucose and *l*-xylose. With *d*-galactose it apparently forms a crystalline derivative with a melting point of 152–155°. With *l*-arabonic and *d*-gluconic lactone no crystalline derivative could be obtained but there was indication of the formation of a crystalline derivative with *d*-mannonic lactone.

### Summary.

This paper describes the preparation and some of the properties of *dl-p-sec.*-butyl-phenylhydrazine; the preparation of *dl-p-sec.*-butyl-aniline, and the resolution of the latter into the *d* and *l* components. The following physical constants are given.

	Boiling point. ° C.	Pressure. Mm.	$\alpha$ in 0.5dm. tube.
<i>dl</i> -Aniline.....	112	11	
<i>d</i> -Aniline.....	123–5	20	+0.26
<i>l</i> -Aniline.....	116.5–118	15	–0.26
<i>dl</i> -Hydrazine.....	155–7	18	
<i>dl</i> -Aniline acetyl derivative.....	125–6		
<i>l</i> -Aniline acetyl derivative.....	123–4	[ $\alpha$ ] <sub>D</sub> = +0.9301.	

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY. No. 380.]

## EXPERIMENTAL STUDIES ON CYSTINE.

BY ALICE R. THOMPSON MERRILL.

Received August 29, 1921.

In preparing cystine for biological experiments it is of importance to know the conditions which favor the precipitation of pure cystine.

It has been shown by Mörner,<sup>1</sup> Embden,<sup>2</sup> Abderhalden<sup>3</sup> and others that cystine may be obtained by the acid hydrolysis of horn, wool and other protein substances containing cystine in combination. When the acid solution is neutralized with alkali or brought to weak acidity with acetic acid after neutralization, the cystine precipitates on standing.

Folin<sup>4</sup> adds sodium acetate to the acid solution of cystine using congo red as indicator. The sodium acetate acts as a buffer salt. He states that this method gives satisfactory results but does not give quantitative difections for the method.

The purpose of this investigation was (1) to determine the concentration of hydrogen ion of solutions of cystine which insures maximum precipitation of cystine; (2) to determine the amounts of sodium acetate to add to the hydrolyzed solution of wool in order to obtain the best yields of cystine and (3) to secure data in regard to purification of the crude cystine from the hydrolyzed solutions. The yield of cystine obtained by Folin's method is compared to the yield obtained by earlier methods.

## Experimental Procedure.

The wool used in this investigation was analyzed and found to contain 3.1% sulfur and 11.6% moisture. Two portions of 750 g. each were boiled with 1500 cc. of conc. hydrochloric acid in separate 3-liter flasks with large necks fitted with reflux water condensers. The solutions in the flasks were heated in oil-baths at a temperature of about 115°. In spite of the condensers, hydrogen chloride fumes poured out through the water-cooled tubes during the first part of the hydrolysis and continued to do so until the acid mixture approached the concentration of the acid-water mixture of constant boiling point. The time of hydrolysis was counted from the time at which all the wool was pushed into the hot acid. The hydrolysis was run for 3 hours, when the biuret test became negative.

The solutions on cooling and thorough mixing had a volume of 4065 cc. and an acidity of 6.9 molar strength. Aliquots of 500 cc. representing 188.0 g. of wool were taken and sodium acetate trihydrate crystals added to each aliquot as shown in Table I. The solutions were heated to boiling

<sup>1</sup> Mörner, *Z. physiol. Chem.*, **28**, 595 (1899).

<sup>2</sup> Embden, *ibid.*, **32**, 94 (1900).

<sup>3</sup> Abderhalden, *ibid.*, **52**, 348 (1907).

<sup>4</sup> Folin, *J. Biol. Chem.*, **8**, 9 (1910).



and boiled for 5 minutes with constant stirring. After standing for 3 days the precipitate of crude cystine was filtered by suction, removed, rubbed up with cold water, filtered and washed once on a Büchner funnel. This process was repeated. The undiluted mother liquors were kept in glass-stoppered bottles and the washings kept separately.

The mother liquors on standing for 2 weeks were filtered by suction and the second precipitates washed and filtered as the first were.

The precipitates were air dried, ground to a powder and kept in desiccators until they came to constant weights.

Sulfur was determined in these weighed precipitates by Osborne's peroxide method. Sulfur was also determined in pure cystine by the Carius method and the results compared with those obtained by the fusion method. It was found that the Osborne method gave results from about 0.2 to 0.3% lower than those obtained by the Carius method on cystine containing 26.69% sulfur. Half-gram samples were fused and an aliquot representing 0.1 g. taken for the precipitation of barium sulfate. Great care was taken to determine and subtract the sulfur in reagents used, to insure barium sulfate precipitates from reduction during ignition and to make determinations in duplicate.

In Table I are shown the grams of sulfur in each precipitate of crude cystine as calculated from the analysis; also the percentages of cystine obtained from the wool. It is considered here that the sulfur determined represents cystine sulfur. This assumption seems correct since these precipitates were almost completely soluble in 1.8 *M* (6.5%) hydrochloric acid and fairly insoluble in cold water as is cystine also, and the yield of pure cystine obtained by experiment corresponds closely to the yield indicated by calculations from sulfur as determined in the crude precipitates.

TABLE I.

SULFUR IN CRUDE CYSTINE PRECIPITATES FROM ALIQUOTS REPRESENTING 188 G. OF WOOL.

NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (3H <sub>2</sub> O). G.	(1) S in 1st ppt. G.	(2) S in 2nd ppt. G.	Total S in 1 and 2. G.	Total sulfur in wool. %.	Total cystine in wool calc. from sulfur found. %.
350	0.077	0.615	0.692	0.368	1.379
450	0.648	0.975	1.623	0.865	3.241
500	1.273	0.746	2.019	1.075	4.028
550	1.260	0.705	1.965	1.046	3.919
650	2.048	0.112	2.160	1.150	4.309
750	2.268	0.055	2.323	1.236	4.631
850	1.706	0.093	1.799	0.957	3.586
950	1.976	0.151	2.127	1.132	4.242

It is evident from Table I that 350 g. of sodium acetate trihydrate precipitated only traces of cystine after standing for 3 days, while 550 g. of sodium acetate gave a yield of only a little over  $\frac{1}{2}$  of the cystine given by 650 g. of acetate; 750 g. of salt gave the maximum yield of cystine.

The sulfur in the precipitates obtained from the mother liquors which stood for 2 weeks after the first filtration was greatest in those in which insufficient sodium acetate had been added to secure good yields of cystine in the first precipitation.

The total yield of cystine in the first and second precipitates from the aliquot in which 500 g. of acetate had been added was almost as large as with greater amounts of sodium acetate, but required 2 weeks' standing instead of 3 days.

### Determination of Hydrogen-ion Concentrations.

In order to determine the concentration of the hydrogen ion more accurately in the cystine solutions, a set of buffer solutions was made up. The acetic acid-sodium acetate mixtures of Walpole<sup>5</sup> were used in place of the potassium hydrogen phthalate solutions recommended by Clark and Lubs,<sup>6</sup> as the latter gave a decided drift when determining the hydrogen-ion concentration by the electrometric method, due possibly to reduction occurring. The set of standard solutions of Clark and Lubs<sup>6</sup> was also made up and used with the one exception stated above. The hydrogen-ion concentrations of these standard buffer solutions were determined directly in the solutions using the hydrogen electrode. By use of the indicators listed by Clark and Lubs the standard solutions were compared colorimetrically with the cystine solutions. It was considered inadvisable to determine the hydrogen-ion concentration in the cystine solutions by the electrometric method because of probable reduction by the hydrogen electrodes.

Since the hydrolyzed solutions were colored dark brown they were diluted to 5 times the original volume as recommended by Walpole.<sup>5</sup> Measured amounts of indicator were added to given volumes of cystine solutions and compared with standard solutions containing the same amount of indicator. That the tints might be comparable the standard solutions plus the indicator were superimposed against the dark solution according to the method of Walpole<sup>7</sup> but modified as follows.

**Modified Comparator Used.**—Difficulty was experienced in the use of the comparator of Humitz, Mayer and Ostenberg<sup>8</sup> due to the reflection of the light from the round sides of the glass tubes. It was believed that glass cells with flat sides and fitted together in pairs would give better results. Four flat-sided glass cells generally used with colorimeters were therefore picked out. These cells were 10×35×53 mm. inner dimensions and were placed together in pairs, the broad sides fitted and held together

<sup>5</sup> Walpole, *J. Chem. Soc.*, 105, 2501 (1914).

<sup>6</sup> Clark and Lubs, *J. Biol. Chem.*, 25, 479 (1916).

<sup>7</sup> Walpole, *Biochem. J.*, 5, 207 (1910).

<sup>8</sup> Humitz, Meyer and Ostenberg, *Proc. Soc. Exp. Biol. Med.*, 13, 24 (1915).

by elastic bands. The cells were filled with solutions and superimposed according to the Walpole combination.

The cells were placed on dull black card board, placed before the screen described by Clark and Lubs<sup>9</sup> and lighted by 4 electric bulbs. A dull black card board with vertical rectangular windows cut close together was drawn over the cells and the color of each as seen through the apertures compared. The cells were also compared in daylight when suitable indicators were used. This substitute for the black box comparator was very satisfactory as well as simple to use.

**Concentration of Hydrogen Ion of Hydrolyzed Solutions.**—Using the modified comparator and brom phenol blue indicator, it was found that the hydrolyzed solution giving maximum yields of cystine after addition of sodium acetate showed a concentration of hydrogen ion equal to  $10^{-4}$ .

It was noticed that congo red gives a red color when sodium acetate is added to a hydrolyzed solution in amounts still insufficient to give maximum yields of cystine, and therefore this red color does not indicate that sufficient sodium acetate has been added.

### Hydrolysis of Wool.

A series of hydrolyses of wool was next made to determine the effect of increasing the length of time of hydrolysis on the yield of cystine. Portions of 500 g. of wool were boiled with 1000 cc. of conc. hydrochloric acid for different periods of time and 750 g. of sodium acetate added to aliquots representing 185 g. of wool. Sulfur was determined in the precipitates formed on standing 3 days and also on precipitates in the mother liquor. Alcohol was also added to the mother liquors until they became turbid, and the precipitates thus formed were analyzed.

TABLE II.

HYDROLYSIS WITH CONCENTRATED HYDROCHLORIC ACID. SULFUR AND CYSTINE IN PRECIPITATES FROM ALIQUOTS REPRESENTING 185 G. OF WOOL.

Time of hydrolysis. Hours.	Sulfur. G.	Calc. cystine in wool. %
3	1.618	3.27
4	2.037	4.12
5	2.120	4.29
6	2.135	4.32
12	2.578	5.22
74	0.120	0.24

A study of Table II suggests that 3 hours' hydrolysis is not a sufficient length of time but that there is an increased yield of cystine up to the 12-hour period. The 74-hour period gives practically no yield of cystine. The addition of alcohol gave a slight increase in yield.

<sup>9</sup> Clark and Lubs, *J. Bact.*, 2, 134 (1917).

Hydrolysis was carried out with 6.8 *M* (22%) hydrochloric acid. Two hundred and fifty g. of wool was boiled with 900 cc. of dil. acid for 12 hours. From an aliquot representing 185 g. of wool only 1.532 g. of sulfur was precipitated, but on adding alcohol until the solution became turbid 1.354 g. of sulfur was further precipitated, giving a total calculated yield of cystine equal to 5.84% of the wool. This indicates that hydrolysis with dilute hydrochloric acid gives good yields of cystine, but as the mother liquors obtained from dilute acid contain less hydrolyzed wool per volume they tend to retain more cystine in solution after neutralization. The advantage of using dil. hydrochloric acid is that while pushing the wool into the hot acid no strong hydrogen chloride fumes are evolved to burn the hands.

### Preparation of Pure Cystine.

The quantitative yields of pure cystine obtained from the crude cystine precipitated by sodium acetate as above were determined.

Two portions of 500 g. of wool were boiled with 1000 cc. of conc. hydrochloric acid each, for 6 hours as usual. Sodium acetate sufficient to give a maximum yield of cystine was added. Each washed and dried precipitate was treated as follows. The precipitate was dissolved in 250 cc. of 1.8 *M* (6.5%) hydrochloric acid, filtered by suction, the insoluble portion digested with 2 portions of 50 cc. of hydrochloric acid and filtered. Norite freed from iron and calcium was added equal to 50 g. on the water-free basis, to the combined filtrates, heated and filtered. The Norite was boiled with 2 portions of 100 cc. of 5% hydrochloric acid<sup>10</sup> and filtered. The filtrates were practically colorless. Five hundred cc. of hot sodium acetate trihydrate solution (1:1) was added to the hot combined acid solution. Almost pure cystine was precipitated. Analysis of the white crystals of cystine showed them to be 98.6% pure. By analysis for sulfur before and after use it was found that the Norite had adsorbed 0.313 g. of sulfur. The yield of cystine thus obtained was 4.3% of the wool and practically equal to the yield as calculated from sulfur determined in the crude precipitate.

### Analysis of Pure Cystine.

Pure cystine was obtained by repeatedly dissolving in 1.8 *M* (6.5%) hydrochloric acid and precipitating with sodium acetate solution. Sulfur in one sample was found by 3 determinations by the Carius method to be 26.66%, 26.63% and 26.86% respectively; the calculated sulfur is 26.69%. By the peroxide method with the same sample 26.37% was obtained.

### Cystine Obtained by the Method used by Abderhalden.

Two hundred and fifty g. of wool was boiled under a reflux condenser with 900 cc. of 6.8 *M* (22%) hydrochloric acid for 12 hours, and evaporated to a gummy mass *in vacuo*. This was dissolved in water, made up to 1000 cc., decolorized with Norite, and 100 g. of sodium hydroxide in solution added to the cold filtrate. After standing for 3 days the fine white crystals were filtered with suction. The concentration of hydrogen ion in the filtrate was found to be  $10^{-4.4}$ . The filtrate was evaporated *in vacuo* and a further yield of cystine obtained.

<sup>10</sup> Miss Dennis recommends that bone-black used in decolorizing these precipitates be boiled with dilute acid. *J. Biol. Chem.*, 9, 369 (1911).

TABLE III.  
CYSTINE BY ABDERHALDEN'S METHOD.

	Sulfur. G.	Cystine. G.	Cystine in Wool. %
1st Ppt.	2.910	10.904	4.36
2nd Ppt.	<u>1.429</u>	<u>5.354</u>	<u>2.14</u>
Total	4.339	16.258	6.50

The total yield of cystine obtained by this method was 6.50% of wool. Here again it is noticed that concentration of the mother liquor results in further precipitation of cystine from solution.

The advantage of using sodium hydroxide solution over that of using sodium acetate is that less salt is formed in the mother liquor and concentration of the latter is easier. In Folin's method the mother liquors are saturated with salt.

### The Determination of the Concentrations of Hydrogen Ion in Solutions in which Maximum Yields of Cystine are Obtained.

The hydrogen-ion concentration of the solutions of hydrolyzed wool which on addition of sodium acetate had given the maximum yield was found to be  $10^{-4}$ .

Of special interest are the results obtained in determining the concentration of hydrogen ion in solutions which give maximum and minimum precipitates of cystine from a solution of pure cystine. Three series were run to obtain these results. In each, 10 g. of pure cystine was dissolved in 1.8 *M* hydrochloric acid and made up to 500 cc. with 1.8 *M* hydrochloric acid.

Fifty cc. aliquot portions containing 1 g. of cystine each were run into separate beakers. Sodium acetate trihydrate in solution (1:1) was added from a buret in various amounts to each beaker and distilled water added to make the volume in each case 150 cc. In another series 4.34 *M* sodium hydroxide solution was added first to 50 cc. of the acetate solution and rinsed with water into the aliquots of cystine solution; the volume was then made up as before to 150 cc. After standing for 48 hours at room temperatures the precipitates formed were filtered into weighed Gooch crucibles with asbestos pads, washed thrice with cold water and once each with alcohol and ether. The precipitates were dried at 100°, cooled in the desiccator and weighed.

The concentration of hydrogen ion was determined in the filtrates kept separate from the washings. Standard buffer solutions, the hydrogen-ion concentrations of which had been determined by the electrometric method, were used for comparison in determining the concentration of hydrogen ion in the filtrates by the colorimetric method.

In Table IV are shown the amounts of reagents used, the percentages of cystine obtained and the corresponding concentrations of hydrogen ion.

The maximum yield of cystine was 96.4%. It is clear that addition of the 1 : 1 sodium acetate solution to 1.8 *M* hydrochloric acid gives a maxi-

TABLE IV.

PERCENTAGES OF TOTAL CYSTINE IN SOLUTION PRECIPITATED AND CONCENTRATIONS OF HYDROGEN ION.

$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ sol. 1 : 1. Cc.	$\text{NaOH}$ 4.34 M. Cc.	Cystine precipitated. %	$\text{Log } C_{\text{H}^+}$
10.0	....	00.00	.....
12.0	....	00.00	.....
14.0	....	00.00	-1.0
16.0	....	11.93	-1.1
16.5	....	16.06	-1.2
17.0	....	53.11	-1.3
17.5	....	62.18	-1.4
18.0	....	75.85	-1.6
19.0	....	93.97	-2.3
20.0	....	96.22	-3.4
30.0	....	96.37	-4.3
40.0	....	96.10	-4.5
50	....	96.29	-4.6
50	18.0	94.54	-6.9
50	18.5	84.91	-8.3
50	19.0	54.64	-8.9
50	19.5	30.77	-8.9
50	20.0	2.67	-9
50	20.5	0.	-9

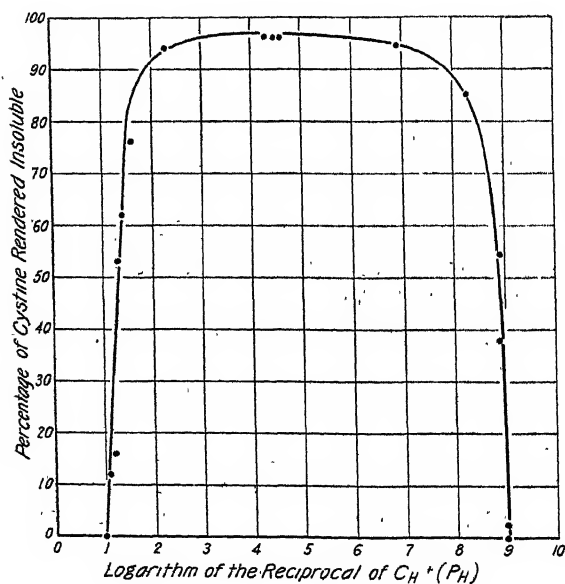


Fig. 1.

imum yield when 20 to 30 cc. of the acetate solution is added to 50 cc. of the dil. hydrochloric acid solution of cystine. As the iso-electric point of tyrosine, calculated from the values  $ka=4\times 10^{-9}$  and  $kb=2.6\times 10^{-12}$  as determined by Kanitz<sup>11</sup> and using the formula<sup>12</sup>  $L=\sqrt{\frac{ka}{kb}}\times kw$  is  $10^{-5.4}$ , it is well to precipitate the cystine at a hydrogen-ion concentration greater than that of  $10^{-5.4}$  to obtain it free from tyrosine.

The curve in Fig. 1 follows the values of Table IV. The iso-electric zone for cystine as indicated is a broad one and shows that cystine can be precipitated in solutions of quite varying strengths.

### Summary.

It has been shown that the zone of hydrogen-ion concentration most favorable for the precipitation of cystine from solution is between  $10^{-3}$  and  $10^{-6}$ . To obtain cystine free from tyrosine it is advisable to precipitate it from solution at a concentration of hydrogen ion of about  $10^{-3}$ .

The quantity of sodium acetate required as a buffer in the hydrolyzed solution of wool was determined. When 100 g. of wool is hydrolyzed with 200 cc. of conc. hydrochloric acid, sp. gr. 1.19, 750 g. of sodium acetate trihydrate crystals should be added to 500 cc. of the hydrolyzed solution to insure maximum precipitation of cystine. The concentration of hydrogen ion was determined and found to be  $10^{-4}$ . The highest yield of cystine thus obtained was 5.2% of the weight of the wool taken.

When sodium hydroxide solution was added to a hydrolyzed solution which had been evaporated *in vacuo* and taken up in water, the yield of cystine obtained was 6.5% of the wool. The filtrate contained less salt than that obtained by Folin's method and could therefore be concentrated with less difficulty. Cystine was obtained pure from the crude cystine precipitated by sodium acetate from the hydrolyzed solution of wool and the percentage yield of pure cystine actually obtained agreed with the yield calculated by determination of sulfur in the crude precipitate.

Comparisons were made between the yields of cystine obtained after boiling wool with conc. hydrochloric acid, sp. gr. 1.19, for from 3 to 12 hours with the yield obtained using 6.8 M (22%) hydrochloric acid for hydrolysis. It was found that boiling wool with conc. hydrochloric acid for 12 hours gave the highest yield of cystine. When about 20% hydrochloric acid was used, the solution was so dilute that alcohol had to be added to the buffered mixture. When alcohol was added, the yield of cystine was as high from the dilute acid hydrolysis as with the concentrated. Dil. hydrochloric acid does not evolve the strong acid fumes that the concen-

<sup>11</sup> Kanitz, *Z. physik. Chem.*, **47**, 476 (1906).

<sup>12</sup> Michaelis and Mostynski, *Biochem. Z.*, **24**, 79-91 (1910).

Michaelis and Davidsohn, *ibid.*, **30**, 143-50 (1911).

trated acid does and is therefore more convenient to handle although it takes more space.

The amount of cystine adsorbed by the Norite used in decolorizing the crude cystine was found to be small when the Norite had been boiled with dil. hydrochloric acid and filtered after decolorizing.

In determining the hydrogen-ion concentration of dark colored solutions a modification was made in the comparator used by Humitz, Meyer and Ostenberg.

The above investigation was suggested by Dr. H. C. Sherman. Appreciation is due also to Dr. A. W. Thomas and Dr. H. T. Beans for helpful advice.

NEW YORK CITY.

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[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY,  
U. S. DEPARTMENT OF AGRICULTURE.]

## THE CHEMICAL COMPOSITION OF CORN OIL.

BY WALTER F. BAUGHMAN AND GEORGE S. JAMIESON.

Received September 1, 1921.

Corn oil is produced from the germ of the corn kernel which is obtained by degerminating corn in the hominy, starch and glucose industries. The germ represents approximately 10% of the dry kernel and contains about 50% of oil. However, the commercially separated germs contain considerable portions from other parts of the corn which reduce the percentage of oil. About 75% of the corn oil output is used after refining for edible purposes. The poorer grades are used for soap making. It has also been used for the preparation of rubber substitutes.<sup>1</sup>

Very little work on the composition of corn oil is reported in the literature. Lewkowitsch<sup>2</sup> states that the unsaturated acids consist of a mixture of oleic and linolic acids and quotes Vulte and Gibson as authority for the statement that the saturated acids consist of palmitic, stearic and arachidic acids. But Hehner and Mitchell<sup>3</sup> could not detect stearic acid. Leathes<sup>4</sup> states that hypogaecic acid occurs in corn oil.

The oil used in this investigation was pressed by means of an oil expeller from corn germs which had been produced by the so-called dry process.

**Physical and Chemical Characteristics.**—The more important physical and chemical characteristics are given in Table I. The saturated and unsaturated acids were determined by the lead-salt ether method.

<sup>1</sup> Sievers, "The Production and Utilization of Corn Oil in the United States," *U. S. Dept. Agriculture Bull.*, No. 904, 1920.

<sup>2</sup> Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan and Co., 5th ed. Vol. 2, p. 168.

<sup>3</sup> Hehner and Mitchell, *Analyst*, 21, 328 (1896).

<sup>4</sup> Leathes, "The Fats," Longmans, Green and Co., 1910, p. 15.



TABLE I.  
PHYSICAL AND CHEMICAL CHARACTERISTICS.

Specific gravity 25°/25° .....	0.9185
Refractive index 20° .....	1.4717
Iodine number (Hanus) .....	117.2
Saponification value .....	187.3
Unsaponifiable matter% .....	1.7 <sup>a</sup>
Acid value .....	2.5
Acetyl value .....	10.0
Saturated acids (determined)% .....	12.3 <sup>b</sup>
Unsaturated acids and unsaponifiable matter (determined)% .....	83.8
Saturated acids (corrected)% .....	11.2
Unsaturated acids (corrected)% .....	82.5
Iodine number of unsaturated acids and unsaponifiable matter .....	136.9
Iodine number of unsaturated acids .....	137.2
<sup>a</sup> Iodine number .....	113.5
<sup>b</sup> Iodine number .....	12.3

Since a complete separation cannot be effected by this method, the percentages of saturated and unsaturated acids have been corrected for the small amount of unsaturated acids, as indicated by the iodine number of the saturated acid fraction, that contaminate and are weighed with the saturated-acid fraction.<sup>5</sup> The content of unsaponifiable matter represents 1.7% of the oil which is about the average figure for corn oil. When separating the saturated and unsaturated acids by the lead-salt ether method the unsaponifiable matter goes with the unsaturated-acid fraction. Therefore the percentage of unsaturated acids has also been corrected for the unsaponifiable matter content of the unsaturated-acid fraction. The iodine number of the unsaponifiable matter is 113.5 and of the unsaturated-acid fraction containing the unsaponifiable matter, 136.9. The iodine number of the pure unsaturated acids is therefore calculated to be 137.2.

**Unsaturated Acids.**—The bromine addition derivatives of the unsaturated acids (and unsaponifiable matter) were prepared by dissolving a portion of the unsaturated-acid fraction, obtained by the lead-salt ether method, which contained 2% of unsaponifiable matter in absolute ether, cooling the solution to 10° and adding bromine slowly after which the solution was allowed to remain for 2 hours at a temperature of 10–15°. No hexabromide, the bromo derivative of linolenic acid which is insoluble in ether, was found. The excess of bromine was removed from the ethereal solution by washing with an aqueous solution of thiosulfate. After drying with anhydrous sodium sulfate the ether was distilled and the residue dissolved in petroleum ether. This solution was allowed to remain overnight in the ice-box and then linolic tetrabromide which had crystallized was removed by filtration through a Gooch crucible.

<sup>5</sup> THIS JOURNAL, 42, 11, 2398 (1920).

<sup>6</sup> Lewkowitsch, Ref. 2, Vol. 1, p. 573.

The filtrate was reduced in volume, cooled in the ice-box and a second crop of tetrabromide crystals obtained and removed by filtration. The filtrate was evaporated to dryness, weighed, and the bromine content determined. This residue contained the oleic dibromide, the linolic tetrabromide that did not crystallize from the petroleum ether and the bromine derivative of the unsaponifiable matter. The iodine number of the unsaponifiable matter is 113.5 which is equivalent to a bromine number of 71.5. The bromine content of the brominated unsaponifiable matter is, therefore, 41.7%. From these data and the theoretical bromine contents of the linolic tetrabromide (53.33%) and oleic dibromide (36.18%) the percentages of tetrabromide and dibromide in the residue were calculated. The data of the analysis of the bromine derivatives are given below.

	G.	%.
Sample of unsaturated acids containing 2% unsaponifiable matter...	3.1035	....
Linolic tetrabromide insoluble in petroleum ether, m. p. 114°.....	2.0170	....
Residue (dibromide, tetrabromide and brominated unsaponifiable matter).....	3.7669	....
Brominated unsaponifiable matter in residue.....	0.1065	....
Bromine content of residue.....		41.7
Bromine content of mixture of oleic and linolic bromine derivatives .....		41.4
Dibromide in mixture of oleic and linolic bromides.....	2.5462	69.6
Tetrabromide in mixture of oleic and linolic bromides.....	1.1142	30.4
Total tetrabromide.....	3.1312	....
Linolic acid equivalent to tetrabromide.....	1.4612	48.0
Oleic acid equivalent to dibromide .....	1.6245	53.4

The percentage composition of the unsaturated acids, also the amounts of oleic and linolic acids and their glycerides in the oil are given below.

Acid.	Found. %.	Calculated to basis of 100%. %.	Original oil. %.	Glycerides in original oil. %.
Oleic	53.4	52.7	43.4	45.4
Linolic	48.0	47.3	39.1	40.9
Total	101.4	100.0	82.5	86.3

The calculated iodine number of the unsaturated acid mixture having the percentage composition represented in Col. 2 is 133.3, while the determined iodine number of the unsaturated acids after correcting for the unsaponifiable matter is 137.2.

**Test for hypogaeic acid,  $C_{16}H_{30}O_7$ .**—This is an unsaturated acid whose melting point is 33–34°. It was tested for by a method similar to that used for testing peanut oil for hypogaeic acid.<sup>7</sup> A 500g. portion of the unsaturated acid fraction was allowed to remain in a cold storage room where a temperature below 0° was maintained for several days. It had been completely solidified and was removed to another room where the temperature was slightly above 0°. After several days most of the

<sup>7</sup> THIS JOURNAL, 43, 6, 1372 (1921).

mass had liquefied. The small amount of solid material that remained was removed by rapid filtration through a previously cooled Büchner funnel. It weighed about 10 mg. After crystallizing from 75% alcohol it melted at 61–62°. This melting point indicates that it consisted chiefly of palmitic acid with enough impurity (stearic acid) present to lower the melting point. It is believed that corn oil does not contain hypogaeic acid.

*Saturated Acids.*—A portion of saturated acids prepared by the lead salt-ether method was esterified with methyl alcohol.<sup>8</sup> The mixture

TABLE II.  
FRACTIONAL DISTILLATION OF METHYL ESTERS OF SATURATED ACIDS.  
(97.0 g. Subjected to Distillation.)

	Fraction.	Temperature °C.	Pressure. Mm.	Weight. G.
	A	157	3	22.0
	B	157–158	3	23.3
	C	159–163	3	23.6
	D	163–175	3	19.3
	E	175–186	3	5.2
	Residue			3.7
				97.1
Fraction A and B distilled	1	153	2.5	7.74
	2	154–156	2.5	22.10
Fraction C added	3	156–159	2.5	23.92
Fraction D added	4	159–164	2.5	20.87
Fraction E added	5	164–173	2.0	12.08
Residue added	6	173–188	2.0	6.04
	7	188–215	2.0	3.90
	Residue			.25
				96.90

of methyl esters was then subjected to fractional distillation under diminished pressure. The data of the distillation are given in Table II. A preliminary distillation was made from a 1-liter Claisen flask, making 5 fractions which are designated by the letters A–E and a residue. The preliminary fractions were redistilled from a 250cc. Ladenburg flask according to the manner indicated in the table. Seven fractions and a residue were obtained.

The iodine numbers which are a measure of the contaminating unsaturated acids and the saponification values of the various fractions are given in Cols. 2 and 3, Table III. Using these data the percentage of unsaturated acids in each fraction was calculated and the saponification values and mean molecular weights corrected accordingly.<sup>9</sup> The mean molecular weights of the saturated acid esters are given in Col. 6.

<sup>8</sup> THIS JOURNAL, 42, 6, 1200 (1920).

<sup>9</sup> *Ibid.*, 42, 152, 1197 (1920).

TABLE III.

RESULTS OF ANALYSES OF FRACTIONS OBTAINED BY DISTILLING METHYL ESTERS OF SATURATED ACIDS.

Fraction.	Iodine number.	Saponification value.	Mean molecular weight.	Esters of unsaturated acids. %.	Mean molecular weight of esters of saturated acids.
1	2.5	204.5	274.3	1.91	273.9
2	2.9	204.0	275.0	2.22	274.6
3	4.5	202.9	276.5	3.44	275.8
4	9.7	200.0	280.5	7.42	279.4
5	17.0	193.1	290.5	13.00	289.8
6	17.9	185.6	302.3	13.69	303.1
7	11.9	165.0	340.0	9.10	345.0
Residue					
Fraction.	Palmitic acid. %.	Stearic acid. G.	Arachidic acid. %.	Lignoceric acid. G.	
1	81.09	6.28	11.98	0.93	.....
2	78.53	17.36	14.26	3.15	.....
3	73.64	17.60	18.01	4.31	.....
4	59.36	12.39	28.57	5.96	.....
5	25.24	3.05	57.55	6.95	.....
9	.....	.....	69.03	4.17	13.28
7	.....	.....	.....	58.15	2.27
Residue	.....	.....	.....	.....	29.04
					1.13
					0.15 <sup>a</sup>
	56.68	25.47	3.07	1.28	

<sup>a</sup> This amount was crystallized from an alcoholic solution of the free acids from the residue.

Inspection of these results indicates what acids may be present in the various fractions. The mean molecular weights of the saturated acid esters in Fractions 1-5 lie between the molecular weights of methyl palmitate (270.3) and methyl stearate (298.4) and indicate mixtures of these two esters. Fraction 6 is probably a mixture of methyl stearate and methyl arachidate (326.4) while the molecular weight of Fraction 7 is consistent with the presence of behenic acid ester but this acid could not be detected when the free acids from this fraction were fractionally crystallized from alcohol so the probable constituents are methyl arachidate and methyl lignocerate (382.5).

In order to test the correctness of these deductions the free acids were recovered from some of the fractions, subjected to fractional crystallization from alcohol and the constituent acids identified by melting-point determinations and elementary analyses. The following acids were identified.

**Lignoceric Acid,  $C_{24}H_{48}O_2$ .**—By fractionally crystallizing the free acids from Fraction 7 a fraction was obtained which melted at 79-80°.

**Analysis.** Calc. for lignoceric acid: H, 13.13; C, 78.18. Found:<sup>10</sup> H, 13.21; C, 78.26.

<sup>10</sup> Analyses by Chas. E. F. Gersdorff.

The free acid preparation obtained from the highly colored residue was dissolved in alcohol and treated with decolorizing carbon. The acid fraction crystallized from this solution weighed 0.15 g. and had a melting point of about 80°. After 4 recrystallizations the melting point was 80–80.5°. There was not sufficient material for an elementary analysis, but the melting point together with the presence of lignoceric acid in Fraction 7 is sufficient evidence to identify it as lignoceric acid.

**Arachidic acid,  $C_{20}H_{40}O_2$ .**—This acid was separated from the Fraction 7 mother liquor from the lignoceric acid crystallization. On one fraction which melted at 76–77° the following analytical results were obtained.

*Analyses.* Calc. for arachidic acid: H, 12.91; C, 76.85. Found:<sup>10</sup> H, 13.22; C, 76.89. Another fraction which melted at 77° had the following composition:<sup>10</sup> H, 13.07; C, 76.73.

**Stearic Acid,  $C_{18}H_{36}O_2$ .**—From Fraction 5 an acid was obtained which melted at 68–69°.

*Analysis.* Calc. for stearic acid: H, 12.76; C, 75.98. Found:<sup>10</sup> H, 12.82; C, 76.05.

**Palmitic acid,  $C_{16}H_{32}O_2$ .**—This acid was isolated from Fraction 1. It melted at 62.5°.

*Analysis.* Calc. for palmitic acid: H, 12.59; C, 74.92. Found:<sup>10</sup> H, 12.30; C, 74.73.

The qualitative composition of the saturated acids having been established the quantitative composition is calculated from the mean molecular weight of the saturated acid esters as determined (Col. 6, Table III) and the theoretical molecular weights of the two esters in each fraction. Thus the percentages and amounts of acids present in each fraction were calculated.

TABLE IV.  
SATURATED ACIDS.

	G.	Percentage composition. %.	Original. %.	Glycerides in original oil. %.
Palmitic	56.68	65.6	7.3	7.7
Stearic	25.47	29.4	3.3	3.5
Arachidic	3.07	3.5	4	.4
Lignoceric	1.28	1.5	.2	.2
	86.50	100.0	11.2	11.8

Table IV gives in Col. 2 the percentage composition of the saturated acids, in Col. 3 the percentage of acids in the original oil, and in Col. 4 the equivalent percentages of glycerides.

### Summary.

The chemical composition of corn oil has been determined with the following results.

COMPOSITION OF CORN OIL.	
Glycerides of.	%.
Oleic acid .....	45.4
Linolic acid .....	40.9
Palmitic acid .....	7.7

COMPOSITION OF CORN OIL (*continued*).

Glycerides of.	%.
Stearic acid .....	3.5
Arachidic acid .....	0.4
Lignoceric acid .....	0.2
Unsaponifiable matter .....	1.7
	<u>99.8</u>

WASHINGTON, D. C.

## NEW BOOKS.

**Pyrometric Practice.** Technologic Paper of the Bureau of Standards, No. 170. By PAUL D. FOOTE, C. O. FAIRCCHILD, and T. R. HARRISON. Government Printing Office, Washington, D. C., 1921. 326 pp. 185 figs. 18 × 25.5 cm. Price \$0.60; from Supt. of Documents.

Only a few years ago the average investigator knew little of pyrometry. The whole subject was a vast mystery to him; he knew something of the use of a mercury thermometer, but a thermocouple, a resistance thermometer, or a radiation-pyrometer would not have been recognized by him, much less understood. To-day the chemist, as well as the physicist and the engineer, is obliged to make frequent and increasing use of one or more of the modern types of thermometer. In the laboratory some form of pyrometer is an indispensable tool; in the plant the size and importance of pyrometric installations has created a new profession, "pyrometric engineering."

This publication is a clear and thorough presentation of the technic of temperature measurement. The authors possess a first-hand knowledge of the subject, and have made frequent contributions to the various branches of pyrometry. The scope of the book is shown by the following list of chapter-headings: Temperature Scale; High-temperature Thermometry; Thermoelectric Pyrometry; General Theory of Optical and Radiation Pyrometry; Optical Pyrometry; Radiation Pyrometry; Resistance Thermometry; Recording Pyrometry; High Temperature Control; Melting-point Methods at High Temperatures; Standardization of Pyrometers; and Industrial Applications of Pyrometry.

As indicated by the title, the book is primarily concerned with the practical side of the subject. It contains "nothing of the historical, and the purely scientific aspects of pyrometry have been intentionally subordinated. It purports to describe practical methods in use in the industries in the year 1920." Nevertheless the theoretical foundations of the various phases of temperature-measurement are recorded, insofar as they are required for a proper understanding of the instruments and methods. While this treatise naturally will find its widest use in connection with industrial installations, it will be helpful to anyone who is called upon to measure temperatures. Of especial value to the research worker is the

chapter on "Melting-point Methods at High Temperatures." The general usefulness of the book would have been enhanced by a description of the deviation-curve and standard-table method of using a thermocouple. The Appendix contains standard tables for the copper-constantan and for the platinum-platinrhodium couples, but no hint is given as to what the tables are used for.

The publication is unusually free from typographical errors. The reviewer noted none, except on p. 170 "enunciator" for "annunciator."

The references are comparatively few; no attempt was made to include a complete bibliography of the subject.

LEASON H. ADAMS.

**Organic Syntheses.** An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. 1. Editorial Board: ROGER ADAMS, Editor-in-Chief, University of Illinois, Urbana, Illinois; HANS THACHER CLARKE, Eastman Kodak Company, Rochester, N. Y.; JAMES BRYANT CONANT, Harvard University, Cambridge, Massachusetts; OLIVER KAMM, Parke, Davis and Company, Detroit, Michigan. John Wiley and Sons, Inc., New York; Chapman and Hall, Limited, London, 1921. vii + 84 pp. 7 fig. 23.5 × 15 cm. Cloth. Price, \$1.50.

This is the first number of a series of pamphlets which the editors propose to issue annually. It is an outcome of the admirable work that was inaugurated by the senior editor when the war cut us off from our largest supply of pure organic chemicals. The main purpose of the series is to supply the investigator with reliable directions for making, in 200g. to 2.5kg. lots, the substances he most frequently needs for his work. In return the authors make the reasonable request that investigators who have had occasion to prepare other organic compounds on a reasonably large scale, report their results for verification and publication in the pamphlets. The authors "hope to make this (series) a clearing house for the exchange of information as to methods of preparation of some of the most needed organic chemicals."

Very few of the methods presented are new, most of them being based on the most satisfactory methods published. Some one of the authors has selected the most promising method, studied it carefully, and prepared a set of directions to be verified or improved by one of the other authors. Only such directions as gave results which were exactly duplicated in both laboratories were deemed ready for publication. The directions are excellent in their definiteness. They specify the best type and size of apparatus to be used, the most favorable temperature, the time required for each step in the process, the precautions that must be taken, the yield of substance sufficiently pure for most purposes, and the best method for getting the purest product. Each preparation is accompanied by explanatory notes and a bibliography which gives references to all of the methods by which the substance has been obtained.

The apparatus specified is in most cases such as is found in any labor-

atory, but the pamphlet also contains descriptions and drawings of some new and ingenious devices that will be found equally useful in other work. The emphasis laid on adequate mechanical agitation is altogether commendable, as is also the substitution of cheap for expensive solvents wherever possible.

The first number describes 23 preparations, selected at random, because the directions for making them happened to be ready for publication. It is expected that each subsequent issue will contain at least 20, and the authors hope that as interest in the work is stimulated this number may be considerably increased. Anyone who has had experience in the preparation of organic compounds on a moderately large scale will appreciate the care and intelligence with which the authors have considered everything that might affect the results.

The pamphlet deserves a wide distribution. For the investigator it is invaluable. The chemical manufacturer will find that most of the methods can be readily developed for production on a larger scale. The instructor in organic chemistry, by cutting down the quantities, will be able to supply his students with directions better than any heretofore available, prepare more interesting as well as more useful substances, and by assigning different preparations in successive years, stock his treasure chest without depleting his purse.

The review hazards the prediction that the new venture will receive such hearty support that the editors will be encouraged to continue the good work. It seems to him that many teachers, whose time and energies are so largely taken up by instruction that protracted systematic research is out of the question, would find it a welcome and profitable diversion to undertake the intensive study of some one preparation and thus contribute to the success of the series.

E. P. KOHLER.



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OF THE

American Chemical Society

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FOR THE YEAR 1921

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EASTON, PA.  
ESCHENBACH PRINTING COMPANY  
1921





# PROCEEDINGS.

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# Proceedings.

## DIRECTORS' MINUTES.

The Directors of the American Chemical Society met at the Chemists' Club, New York City, on December 11, 1920, at 3 P.M., with Directors Noyes, Bancroft, Barnard, Bigelow, Little, Teeple and Parsons present.

In reply to a request that arrangements be made whereby members could obtain bound volumes of the journals, the Directors voted that it was in their opinion impracticable to arrange for such binding.

The Treasurer reported to the Directors that on November 9th he had borrowed, at 6%, \$12,000 and on November 24th, \$7,000 to meet the expenses of the Society, as per authority given him by the Directors, and that these loans had been paid by him on December 9th. This action of the Treasurer was officially approved.

It was voted that the safety deposit box of the American Chemical Society, No. 1641, in the Farmers' Safe Deposit Company may be entered only by the Treasurer in the presence of such member of the Finance Committee as the Treasurer may from time to time designate in writing.

It was voted to appropriate \$500 to the Annual Tables of Constants and Numerical Data.

It was voted to print a Directory during 1921, but to omit the geographical portion thereof.

It was voted that the Treasurer be authorized to spend up to \$500 from Incidental Account for furnishing a booth at the Chemical Exposition in 1921 if in his judgment it is wise to do so.

In view of a letter received from Mr. E. J. Crane, Editor of *Chemical Abstracts*, protesting against the wording of a resolution passed by the University of Illinois Section of the American Chemical Society, criticising the conduct of *Chemical Abstracts*, the Directors unanimously voted to instruct the Secretary to inform the Editor of *Chemical Abstracts* that the Directors, and in their belief the Council and most of the members of the Society, are entirely satisfied with his conduct of that *Journal* and to express their high appreciation of the efficient and competent manner in which he and his associates have handled that *Journal*, often with inadequate facilities, since he has been in charge of its affairs.

The proposed budget for 1921 was then carefully considered and was finally adopted as follows:

## INCOME (1921).

Dues.....	\$207,000.00
Subscriptions.....	20,000.00
Back Numbers.....	5,000.00
Reprints.....	1,600.00
Postage.....	3,000.00
December Index.....	1,000.00
	<hr/>
	\$237,600.00
Advertising.....	90,000.00
Interest.....	7,000.00
	<hr/>
	\$334,600.00

## EXPENSE (1921).

*Journal American Chemical Society:*

Editor.....	\$ 1,500.00	
Clerical and Office.....	1,600.00	
2900 Pages of Printing.....	47,500.00	
	<hr/>	\$50,600.00

*Chemical Abstracts:*

Editor.....	\$ 4,500.00	
Assistant Editor's Salary.....	2,750.00	
Second Assistant Editor's Salary.....	1,800.00	
Abstractors and Assistant Editors.....	9,800.00	
Clerical.....	4,500.00	
Expenses.....	1,100.00	
Formula Index.....	2,500.00	
4600 pages of Printing.....	76,800.00	
	<hr/>	\$103,750.00

*Industrial Journal:*

Editor's Salary.....	\$10,000.00	
Assistant Editor.....	3,000.00	
Clerical.....	7,400.00	
Staff Correspondents.....	4,880.00	
Office Expense.....	2,300.00	
Traveling Expense.....	1,000.00	
1200 Pages of Printing.....	47,800.00	
Rent.....	4,167.00	
	<hr/>	\$80,547.00

*News Service*

Salary.....	\$5,000.00	
Expense.....	3,790.00	
Traveling Expense.....	1,000.00	
Clerical.....	3,040.00	
Rent.....	833.00	
	<hr/>	\$13,663.00

*Advertising:*

Printing Advertisements.....	44,560.00
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*Scientific Monographs.*

Salary.....	1,000.00
Expense.....	125.00

Technological Monographs,		
Salary .....	\$1,000.00	
Expense.....	25.00	
		\$2,150.00
Secretary's Office:		
Salary .....	\$5,000.00	
Clerical.....	10,300.00	
Expenses.....	4,500.00	
Rent.....	1,152.00	
		\$20,952.00
Treasurer's Office		
Salary .....	\$1,000.00	
Clerical.....	1,700.00	
Expenses.....	1,000.00	
		3,700.00
President's Office:		
Traveling Expense.....	\$1,000.00	
Expense.....	200.00	
		1,200.00
Back Numbers.....	\$4,000.00	
Local Sections.....	8,500.00	
Incidentals.....	2,000.00	
General Meetings.....	2,000.00	
Directory.....	2,000.00	
Table Physical Constants.....	500.00	
		19,000.00
Total.....		\$340,122.00

CHARLES L. PARSONS, *Secretary*.

### COUNCIL.

The following communication was sent to the Council on December 1st:

AMERICAN CHEMICAL SOCIETY.

December 1, 1920.

*Council of the American Chemical Society:*

GENTLEMEN:—The following members have been duly nominated for the offices indicated for the years 1921 and 1921–1923. Kindly check your choice with an X and return the ballot on or before December 21st.

Please note that by vote of the Council the names are arranged in alphabetical order and not in the order of the nominating vote.

Very truly yours,

CHARLES L. PARSONS, *Secretary*.

*President*.—1921 only (one to be chosen) (alphabetically arranged): R. F. Bacon, E. C. Franklin, Edgar F. Smith, H. P. Talbot.

*Directors*—1921–1923, inclusive (two to be chosen) (alphabetically arranged): H. E. Barnard, A. V. H. Mory, G. D. Rosengarten, H. P. Talbot.

*Councilors-at-Large*.—1921–1923, inclusive (four to be chosen. Ballot is void unless four are voted for) (alphabetically arranged): G. P. Adamson, C. L. Alsberg, H. E. Howe, L. W. Jones, C. E. K. Mees, A. V. H. Mory, J. F. Norris, Allen Rogers.

The returns of this ballot were counted on the evening of December 21 by a committee consisting of Leo Finkelstein, L. I. Shaw and Charles L. Parsons, and the following officers were elected:

*President*, Edgar F. Smith.

*Directors*, George D. Rosengarten and H. P. Talbot.

*Councilors-at-Large*, C. L. Alsberg, H. E. Howe, L. W. Jones, Allen Rogers.

CHARLES L. PARSONS, *Secretary*.

MEMBERS ELECTED BETWEEN NOVEMBER 15 AND DECEMBER 15, 1920.

- Abramson, Samuel, 39 Schuyler St., Roxbury, Mass.  
 a Brassard, Fred, F. a Brassard & Crawford, Wakefield, Yorks, England.  
 Allen, Monica M., 602 Monroe, Ann Arbor, Mich.  
 Andrews, Andrew I., 615 N. Lake St., Madison, Wis.  
 Angel, Edward Reeve, Gresham Lodge, Streatham Common, London, S. W. 16, England.  
 Auden, Harold A., 18 Paisley St., Liverpool, England.  
 Badger, Cecil H., Hyattsville, Md.  
 Bailey, Austin, 211 Chemung St., Corning, N. Y.  
 Baker, Chester P., 53 Wendell Ave., Brockton, Mass.  
 Baker, Howard, 214 N. Lombard Ave., Oak Park, Ill.  
 Baker, Julian L., Dial Cottage, Cookham Road, Maidenhead, Berks., England.  
 Balyozian, Nicholas, 828 Blue Hill Ave., Dorchester, Mass.  
 Bartkus, Joseph, 8811 Superior Ave., Cleveland, O.  
 Basinow, Maurice, 154 Humboldt Ave., Roxbury, Mass.  
 Bawden, Arthur T., 31 Chittenden Ave., Columbus, O.  
 Beeaker, Stephen W., Phi Eta Kappa House, Orono, Me.  
 Bell, Thomas G., P. O. Box 331, Borosolvay, Cal.  
 Bernstein, Abraham J., 549 East 139th St., New York, N. Y.  
 Birchard, Frederick J., Postal Sta. B, Dominion Grain Research Lab., Winnipeg, Canada.  
 Bishop, James A., 1265 Lafayette St., Denver, Colo.  
 Blake, John T., 102 Hewlett St., Roslindale, Mass.  
 Blinn, H. M., 110 Commerce St., Baltimore, Md.  
 Blumenstiel, Monroe A., 204 Dartmouth St., Rochester, N. Y.  
 Bolan, Robert S., California Inst. of Tech., Pasadena, Cal.  
 Boulden, J. S., 5559 Pershing, St. Louis, Mo.  
 Bradley, Robert B., 58 Freeman St., Newark, N. J.  
 Brandt, Russell W., The Maury, 19th & G Sts., N. W., Washington, D. C.  
 Branham, B. T., c/o National Cannery Association, Bridgeton, N. J.  
 Braunscholtz, W. T. K., "Goslar," Adams Rd., Cambridge, England.  
 Brentnall, Blanche, 2001 East Elm, East Enid, Okla.  
 Bridges, Frank L., 36 Parker Hall, Lewiston, Me.  
 Broughall, Laurence St. C., Woodview, Hadley, Barnet, Herts, England.  
 Bunbury, Hugh M., Dudley Lodge, Prestwich, Manchester, England.

- Butler, Freeman P., 99 Salisbury St., Worcester, Mass.  
 Burns, James E., 93 Moore St., Lowell, Mass.  
 Cameron, Iain, National Tar Products, Ltd., Barrhead, Scotland.  
 Campbell, C. G., Kewaunee, Wis.  
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## MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons,  
1709 G St., N. W., Washington, D. C.]

### CALIFORNIA SECTION.

The 119th regular meeting of the Section was held on December 3, at the Engineers' Club, San Francisco. Papers were read as follows: "Some Improvements in Fractional Distillation," by S. W. Young of Stanford University, and "A Short History of the Chlorine Industry, by Ludwig Rosenstirn, of the Great Western Electric Chemical Co. The attendance at this meeting was 25 per cent. of the total membership.

The following officers were elected for the ensuing year:

William C. Bray, *Chairman*; Bryant S. Drake, *Vice-Chairman*; Lloyd W. Chapman, *Secretary-Treasurer*; Joel Hildebrand, Lionel H. Duschak, Ralph A. Gould, and Robert E. Swain, *Councilors*.

LOYD L. CHAPMAN, *Secretary*.

### CINCINNATI SECTION.

The 238th regular meeting of the Section, held on December 8 in the Chemistry Auditorium of the University of Cincinnati, was addressed by F. M. Callender, of Parke, Davis & Company, on "Standardization of Drugs."

C. H. LUND, *Secretary*.

### CLEVELAND SECTION.

At the meeting on November 5, the following officers for 1921 were elected: L. C. Drefahl, *Chairman*; W. R. Veazey, *Vice-Chairman*; H. S. Booth, *Secretary-Treasurer*; H. D. Batchelor, W. M. Clark, H. Gruener, B. C. Goss, W. R. Mott, N. K. Chaney, *Board of Managers*; R. D. Landrum, A. W. Smith, Hugo Schapiro, and H. E. Simmons, *Councilors*.

WM. ROY MOTT, *Secretary*.

### COLORADO SECTION.

S. C. Lind, of the U. S. Bureau of Mines, Golden, Colo., read a paper on "The Disruption of the Atoms and the Possibility of Transmutation of the Elements," before the Section, November 22.

The Section held a banquet on Wednesday evening, December 15, at the Hotel Metropole, Denver, Colo.

RUTH B. VORTREES, *Secretary*.

### CONNECTICUT VALLEY SECTION.

On December 11, Harold Hibbert, of Yale University, spoke before the Section on "The Constitution of Cellulose."

HARRY WESSELS, *Secretary*.

### CORNELL SECTION.

At the regular meeting, held on December 1, W. W. Rowlee addressed the Section on "Chemical Botanical Problems."

On December, 15, Sutherland Simpson spoke before the Section on "Chemical Control in the Body."

F. R. GEORGIA, *Secretary.*

#### DELAWARE SECTION.

On December 22, Joseph S. Ames, professor of physics, Johns Hopkins University, spoke before the Section on "Relativity."

FRED C. ZHISBERG, *Secretary.*

#### EASTERN NEW YORK SECTION.

On December 17, James Kendall, of Columbia University, addressed the Section on the subject, "A Modified Ionization Theory."

MARY R. ANDREWS, *Secretary.*

#### GEORGIA SECTION.

J. L. McGhee, of Emory University, addressed a called meeting of the Section, November 19, on the subject, "Osmotic Pressure."

J. S. BROGDON, *Secretary.*

#### INDIANA SECTION.

At the regular meeting of the Section, held on December 10, the following addresses were given: "Some Problems of the Canning Industry," by John P. Street, director of Indiana Inspection Service, National Canners Association; and "Some Things a Chemist Should Know about Patents," by George G. Schley, *Patent Attorney.* Attendance, 31%.

EDGAR B. CARTER, *Secretary.*

#### LEHIGH VALLEY SECTION.

The following program was given before the Section at its meeting held at Palmerton, Pa., on December 4: "New Instruments for Paint Testing," by A. H. Pfund, of Johns Hopkins University; "Industrial Microscopy," by H. Green, and "Research Progress," by F. G. Breyer, of the Research Division, New Jersey Zinc Co. Attendance 33-47%.

JOHN T. LITTLE, *Secretary.*

#### LEXINGTON SECTION.

The 65th meeting of the Section was held at the University of Kentucky on November 23, when C. S. Crouse, of the University, spoke on "Oil Shales of Kentucky."

The 66th meeting was held on December 15 at the University of Kentucky. A paper entitled, "A Rapid Method for the Analysis of Dolomite and Magnesian Limestones," was presented by S. D. Averitt. A report on the annual convention of the Association of Official Agricultural Chemists was made by R. H. Ridgell. Attendance, 45%.

O. M. SHEDD, *Secretary.*

#### LOUISIANA SECTION.

The regular monthly meeting of the Section was held on November 16, at which time Dr. Wm. A. Noyes, President of the American Chemical Society, spoke on "The Foundations for Chemical Development."

CASSIUS L. CLAY, *Secretary.*

## MARYLAND SECTION.

The 45th regular meeting of the Section occurred on December 1, in the Chemical Laboratory Lecture Room of Johns Hopkins University. Davis I. Macht, of the Johns Hopkins Medical School, spoke on the "Relation of the Chemical Structure of the Opium Alkaloids to their Physiological Action." Dr. Macht also touched on the "Synthetic Substitutes of the Opium Alkaloids." 25% of the membership was in attendance.

C. CLIFTON HOWES, *Secretary*.

## MICHIGAN AGRICULTURAL COLLEGE SECTION.

The meeting of the Section on December 11 was held at the Hotel Kerns, Lansing, Mich., when William McPherson, head of the Department of Chemistry and dean of the Graduate School in Ohio State University, spoke to the members. Attendance, 93%.

BRUCE E. HARTSUCH, *Secretary*.

## MILWAUKEE SECTION.

The Chicago and Milwaukee Sections engaged in an indoor baseball game at the Milwaukee Athletic Club on November 20, at 4.45 P.M. Following the banquet in honor of the visiting guests, short talks on industrial subjects were given by members of both Sections.

On December 3, J. D. Mathews, of the University of Wisconsin, spoke before the meeting of the Section, his subject being, "Photo-Chemistry."

WM. KLOPPENBURG, *Secretary*.

## NASHVILLE SECTION.

Wm. D. Harkins, professor of Physical Chemistry in the University of Chicago, addressed the meeting of the Section, which occurred on November 18, on the subject, "Atoms and How They are Built."

H. A. WEBB, *Secretary*.

## NEBRASKA SECTION.

On December 14, Ernest Anderson, for three years in the Transvaal University College of South Africa, spoke before the Section on "Some Chemical Problems Peculiar to South Africa."

B. CLIFFORD HENDRICH, *Secretary*.

## NEW HAVEN SECTION.

At the regular meeting of the Section, held on December 14, C. R. Hoover, of Wesleyan University, spoke on "The Detection of Small Amounts of Carbon Monoxide."

BLAIR SAXTON, *Secretary*.

## NEW YORK SECTION.

At the meeting of the Section held on December 10, Hugo S. Taylor spoke on the subject, "The Mechanism of Catalytic Processes."

HERBERT G. SIDEBOTTOM, *Secretary*.

## NORTHEASTERN SECTION.

The 162nd regular meeting of the Section occurred on December 10, at the Engineers' Club, Boston, Mass., when W. T. Bovie, assistant

professor of biophysics at the Medical School of Harvard University, spoke on "The Structure of Protoplasm in the Light of the Electron Theory of Matter."

L. F. HAMILTON, *Secretary*.

#### OKLAHOMA SECTION.

The second annual meeting of the Section was held on November 19 and 20, at Stillwater, Okla. The following program was carried out: November 19.—"The Foundations for Chemical Development," by Wm. A. Noyes, president of the American Chemical Society. November 20.—Presidential address, by Edwin Debarr; "The Production of Cylinder Stocks from Oklahoma Crudes," by Sidney Born; "The Nitrogen Distribution of the Alkali-Soluble Proteins of Cottonseed Meal," by W. G. Friedmann; "Milk," by Edwin Debarr; "The Preparation of Glycollic Acid," by Hilton Ira Jones; and "Positive and Negative Valence," by W. A. Noyes. The business meeting and annual election of officers occurred at the close of the program.

HILTON IRA JONES, *Secretary*.

#### PHILADELPHIA SECTION.

At the regular monthly meeting of the Section, held on December 16, the following program was presented: "The Receptivity of Dyes to Proteins," by George Heyl, of Heyl Laboratories, New York City; and "Arsphenamin," by George W. Raiziss, of the Philadelphia Dermatological Institute.

J. HOWARD GRAHAM, *Secretary*.

#### PUGET SOUND SECTION.

At the meeting of the Section held on December 9, F. R. Heath, of the Chemistry Department, University of Washington, addressed the members on "Phosphorescent Substances." The annual election of officers occurred at this meeting.

ROBT. T. ELLIOTT, *Secretary*.

#### ROCHESTER SECTION.

The 113th regular meeting of the Section, on November 23, was addressed by Richard B. Moore, chief chemist of the U. S. Bureau of Mines, on the subject, "Helium, Its History, Preparation and Uses." The members of the Science Section of the New York State Teachers Association were guests at this meeting. Membership attendance was 66-2/3 per cent.

On December 6, a joint meeting between the Local Section and the Optical Society of America, Rochester Section, was held at the University of Rochester. L. A. Jones, of the Eastman Kodak Company, gave an illustrated lecture on "Measurement and Specification of Color."

ERLE M. BILLINGS, *Secretary*.

#### SAVANNAH SECTION.

The Section began its active fall and winter work with a meeting on November 22, when H. S. Bailey gave a review of the Council meeting and session of the Society at Chicago. R. F. Monsalvatge covered the entertainments and industrial trips provided for the visiting chemists

at Chicago. This was followed by a report on the Chemical Industries Exposition in New York, by V. H. Bassett. Attendance, 40 per cent.

#### ST. LOUIS SECTION.

R. D. Oilar, of the Brecht Company, gave an illustrated lecture on December 6, before the Section, taking as his subject "Vegetable Oil Industries."

T. R. BALL, *Secretary*,

#### SOUTHEAST TEXAS SECTION.

At the 15th meeting of the Section, held on December 11, R. G. Upton, City Sanitary Engineer of Port Arthur, addressed the members on the subject, "The Work of a City Chemist."

P. S. TILSON, *Secretary*.

#### SOUTH JERSEY SECTION.

On December 8, Allen Rogers, of Pratt Institute, spoke before the fifth regular meeting of the Section on the subject, "Shark Fishing and Shark Leather."

C. E. BURKE, *Secretary*.

#### SYRACUSE SECTION.

The 144th regular meeting of the Section occurred on November 19. Thomas W. Pritchard, of Columbia University, spoke on "The Whitaker-Pritchard Process of Destructive Distillation."

The 145th regular meeting, held on December 17, was addressed by Ellwood Hendrick, of New York, on "Relativity and Life." Attendance, 25%.

B. W. GRIMES, *Secretary*.

#### TOLEDO SECTION.

The regular monthly meeting of the Section was held on December 13. Oliver Kamm, director of the Chemical Research Department of Parke, Davis & Co., Detroit, Mich., gave a paper on "Organic versus Inorganic Analysis." Announcement is made of the publication of the first directory of the Section.

R. W. ERWIN, *Secretary*.

#### UNIVERSITY OF ILLINOIS SECTION.

At the regular meeting of the Section on November 16, the following officers for the year 1921 were elected: Roger Adams, *Chairman*; L. H. Smith, *Vice-Chairman*; S. A. Braley, *Secretary*; J. H. Reedy, *Treasurer*; G. D. Beal and E. W. Washburn, *Councilors*. A paper on "Energy from the Bacteriologist's Viewpoint," was presented by F. W. Tanner.

S. A. BRALEY, *Secretary*.

#### UNIVERSITY OF MICHIGAN SECTION.

F. E. Bartell gave a paper on "Anomalous Osmose and its Relation to the Behavior of Certain Colloid Systems," before the regular meeting of the Section, held on November 30.

R. J. CARNEY, *Secretary*.

#### UNIVERSITY OF MISSOURI SECTION.

The 95th meeting of the Section was held on December 3, when H. E. Patton, of St. Louis, gave an address on "Reality as a Factor in Research." Attendance, 100 per cent.

H. D. HOOKER, JR., *Secretary*.

## VIRGINIA SECTION.

The 37th meeting of the Section, on November 19, had as its speaker, Graham Edgar, professor of chemistry at the University of Virginia, whose subject was, "Architecture of the Atom." Attendance, 50 per cent.

The 38th meeting of the Section was held on December 17. A lecture illustrated by lantern slides, on the subject, "The Physics of Flying," was delivered by Robert E. Loving, professor of Physics at Richmond University.

ROBERT F. McCracken, *Secretary*.

## WASHINGTON, D. C., SECTION.

On November 11, the following officers of the Section were elected: William Blum, *President*; J. B. Reed, *Secretary*; F. P. Dewey, *Treasurer*; W. M. Clark, W. D. Collins, A. Seidell, F. W. Smither, and R. B. Sosman, *Councilors*.

The 312th meeting was held on December 9, when the following program was given: "Petroleum Products," by J. P. Lewis; "Coal Tar Products," by W. M. Rile; "Industrial Alcohol," by B. R. Tunison; and "Forest Products," by E. C. Sherrard.

J. B. REED, *Secretary*.

## WISCONSIN SECTION.

At a special meeting of the Section, held on November 23, Frederick G. Cottrell, director of the U. S. Bureau of Mines, spoke on "Commercial Liquefaction and Separation of Gases."

On December 15, Arthur I. Kendall, dean of the Medical School, Northwestern University, spoke before the Section on "Bacteria as Chemical Reagents."

JOHN H. SCHMIDT, *Secretary*.

## DECEASED.

Drew, Dr. Charles W., 322 Fourth St., South Minneapolis, Minn. Died, November 25, 1920.

Dreyfus, Louis A., Maple Ave., Rosebank, S. I., N. Y. Died, December, 1920.

Eberly, H. W., Atlas Powder Co., Lansing, N. J. Died, Oct. 16, 1920.

Farnsworth, J. P., 52 Valley St., Providence, R. I. Died, Dec. 3, 1919.

Massey, J. R., Glass Founders Corp., Milftown, N. J. Died, Nov. 19, 1920.

Rowley, Walter E., 21 Burling Slip, New York City. Died Oct. 9, 1920.

Surface, Henry Earl, Valuation Engineer in Forest Industries, Washington, D. C. Died, June 9, 1920.



# Proceedings.

## Report of the Secretary of the American Chemical Society for the Year 1920.

The growth of the American Chemical Society during the year 1920 has again been large. The society has made a net gain of 1,896 members during the year. The membership of the Society at the end of 1919 was 13,686. It was 15,582 on December 31, 1920. Statistics follow:

Honorary members.....	9
Life members.....	21
Corporation members.....	99
Members.....	15,453

Total, Dec. 31, 1920..... 15,582

During the year one honorary member, Dr. Ernest Solvay, was added.

The number of members now in arrears registered in the Local Sections on November 30, 1919, was 10,306; the number on November 30, 1920, was 11,623. The number in each Section for 1919 and 1920 is noted below:

Local section.	Number of paid mem- bers, 1919.	Number of paid mem- bers, 1920.	Cash retained from balance, 1919.	Total Dr. account 1920.
Alabama.....	54	63	\$47.89	\$67.50
Ames.....	32	36	.06	50.06
California.....	333	370	...	200.00
Central Texas.....	57	60	...	50.00
Chicago.....	694	892	...	520.50
Cincinnati.....	230	248	83.06	200.00
Cleveland.....	376	411	31.14	282.00
Colorado.....	...	111	...	22.98
Columbus.....	96	101	...	100.00
Connecticut Valley.....	101	114	...	100.00
Cornell.....	45	51	0.16	50.16
Delaware.....	363	258	0.38	200.38
Detroit.....	129	148	...	155.00
Eastern New York.....	82	98	83.98	83.98
Georgia.....	73	50	...	25.00
Indiana.....	181	208	...	181.00
Iowa.....	67	77	31.23	81.23
Kansas City.....	158	195	71.40	158.00
Lehigh Valley.....	136	123	...	136.00
Lexington.....	26	27	...	50.00
Louisiana.....	56	73	1.46	70.00
Louisville.....	25	30	...	...
Maine.....	57	55	...	25.00
Maryland.....	201	231	27.22	150.75

Social section.	Number of paid mem- bers, 1919.	Number of paid mem- bers, 1920.	Cash retained from balance, 1919.	Total Dr. account, 1920.
Michigan Agricultural College...	28	30	...	50.00
Midland.....	30	36	...	...
Milwaukee.....	114	155	...	142.50
Minnesota.....	138	151	77.81	138.00
Nashville.....	32	34	15.30	40.30
Nebraska.....	52	40	46.64	46.64
New Haven.....	94	94	...	75.00
New York.....	1,990	2,213	46.62	1,446.62
North Carolina.....	57	51	1.46	26.46
Northeastern.....	772	847	90.40	579.00
Northern Intermountain.....	18	27	8.00	33.00
Oklahoma.....	77	112	...	96.25
Omaha.....	...	50	...	50.50
Oregon.....	39	45	52.50	52.50
Philadelphia.....	749	771	...	550.00
Pittsburgh.....	494	513	42.09	317.09
Puget Sound.....	107	103	10.35	133.75
Rhode Island.....	99	106	5.70	123.75
Rochester.....	81	134	...	100.00
St. Louis.....	187	222	...	187.00
Savannah.....	...	32	...	25.00
South Carolina.....	21	27	36.85	36.85
South Dakota.....	27	23	3.60	43.60
South Jersey.....	...	85	...	81.25
Southeast Texas.....	43	59	24.61	64.50
Southern California.....	179	242	9.02	179.00
Syracuse.....	173	143	11.04	173.00
Toledo.....	52	68	1.73	73.50
University of Illinois.....	127	139	61.54	155.00
University of Michigan.....	54	62	12.12	37.12
University of Missouri.....	19	26	28.21	28.21
Vermont.....	19	24	42.12	42.12
Virginia.....	90	107	23.96	112.50
Washington, D. C.....	383	379	90.35	287.25
Western New York.....	273	305	...	204.75
Wisconsin.....	116	138	10.42	110.42
	10,306	11,623	\$1,130.42	\$8,801.97

The table gives a summary of the sectional accounts for the year, shows the number of members in each Section for 1919 and 1920, the funds held over from 1919 account, and the total funds (which include the balances) charged to the 1920 account.

During the year the Society added the Colorado, Omaha, Savannah and South Jersey Sections to its Local Sections.

During the past two fiscal years, December 1, 1918, to November 30, 1920, the Secretary has made collections as follows:

	1919.	1920.
Membership dues or subscription.....	\$125,428.00	\$140,482.00
Subscriptions .....	13,208.72	15,863.98
Back numbers.....	5,765.54	9,127.02
Reprints.....	1,305.31	1,626.81
Postage.....	2,878.65	3,719.05
Interest.....	802.63	659.87
Exchange and miscellaneous.....	137.78	26.41
Directory.....	140.75	18.00
Decennial Index to Chemical Abstracts.....	1,898.25	1,699.00

\$151,565.63    \$173,222.14

These amounts were duly transmitted to the Treasurer of the Society.

Subscriptions and the sale of back numbers during the past year have again increased.

Several complete sets of our journals have been sold to foreign and domestic libraries and several incomplete sets have been added to by the purchase of odd volumes where they could not be furnished from the stock. The stock has been kept in good condition by the purchase of numbers needed to complete full volumes, but sets are now hard to obtain, as many volumes are already sold out or are nearing exhaustion.

Back numbers are mailed direct from Easton, Pa., on orders sent through the Secretary's office. The following is a summary of the back numbers sent out by the Secretary during the year, together with the present stock of journals:

Copies of the Society's publications sent out from January 1, 1920, to December 31, 1920, aside from mailing lists.....	64,958
Copies of the Jour. Amer. Chem. Soc. in stock.....	18,840
Copies of Chemical Abstracts in stock.....	17,498
Copies of the Jour. Ind. & Eng. Chem. in stock.....	17,626
Copies of the General Index, Vols. 1-20, J. A. C. S. in stock.....	75
Copies of Anniversary Number in stock.....	92
Volumes of Decennial Index in Stock.....	381

The Society has grown in influence in even more rapid degree. It has been very influential in passing important chemical legislation which is beneficial not only to the Society but to the country at large. The American Chemical Society News Service is being received regularly by several hundred publications throughout the country and its bulletins are widely reprinted. The average salaries of chemists have increased during the last few years probably to a greater extent than any other profession. There is no technical profession in the world where the members are so united and where they work so as a unit for the development of their science as do the chemists of America. There has never been a time in the history of the world when chemists and the chemical profession were appreciated by the public as they are to-day. Two successful general meetings were held during the year, one at St. Louis and one at Chicago,

and both had an inspiring effect upon the chemical life and chemical thought of their communities. The Dye Chemistry Section has become a large, enthusiastic and active Dye Chemistry Division. Sections of Sugar Chemistry, Cellulose Chemistry and Leather Chemistry have been formed and are rapidly proving their worth and the probable future need of divisions in these special lines of endeavor. The Colorado, Omaha, Savannah, and South Jersey Sections have been added to our Local Sections during the year. The Board of Editors of Scientific and Technological Monographs have begun active work and important books bearing the emblem and the backing of the American Chemical Society will shortly be issued as the first of a series of American Chemical Society Chemical Monographs. The first, "The Chemistry of Enzyme Action," is now in press. Our journals are increasing daily in importance and recognition throughout the world. The *Journal of Industrial and Engineering Chemistry* is being recognized more and more as the most valuable advertising medium in the world to reach chemists and the chemical industries, and its advertising has grown so large and so important that it has now been turned over to a competent, hustling firm to handle. Plans are already under way for an important general meeting in Rochester, April 26 to 29, 1921, and for a world-wide gathering of chemists in New York in the early days of September, when the British Society of Chemical Industry will come down from its general meeting in Canada to meet with its New York Section, with the American Chemical Society, with the Seventh National Exposition of Chemical Industry, and with other bodies of chemists that may desire to meet in New York City at that time. The year 1921 promises to be a banner year for the American Chemists and American Chemical Industry.

The Secretary wishes to express his appreciation for the continued assistance and loyal support of members of the Society. Without their aid little could be accomplished. Respectfully submitted,

CHARLES L. PARSONS, *Secretary*.

### Report of the Editor of the Journal of the American Chemical Society for the Year 1920.

The number of papers and book reviews and the number of pages devoted to them in the JOURNAL during the past five years have been as follows:

	Number.					Pages.				
	1916.	1917.	1918.	1919.	1920.	1916.	1917.	1918.	1919.	1920.
Proceedings.....	...	...	...	...	...	109	173	112	162	168
Physical and Inorganic.	161	136	114	107	180	1618	1243	1023	1053	1695
Organic and Biological..	146	164	106	116	122	1265	1482	906	1089	936
Book Reviews.....	41	37	21	29	54	41	30	30	31	59
Total.....						2933	2928	2071	2335	2858

There has evidently been a marked increase in the size of the JOURNAL as compared with last year. Indeed, the pre-war figures were almost attained, so that the prediction made in the last Report has been emphatically fulfilled. This increase occurred in spite of still greater insistence on conciseness and brevity of presentation. This insistence did, however, have the effect of reducing the average length of the articles from 9.1 in 1916 and 17; 9.5 in 1918, and 9.6 in 1919, to 8.7 pages during the past year. On the basis of these figures and the present influx of new manuscripts, it is probable that a still further increase will occur during the coming year, unless further restrictive measures are adopted.

During the past year the resignation of Dr. Marston T. Bogert from the Editorial Board was reluctantly accepted. Dr. Bogert has served the Society faithfully, wisely, and unselfishly as Associate Editor for many years. The Editor wishes to express appreciation and gratitude on his own behalf and on that of the Society for this service. The Editor also wishes to report the election during the past year of Dr. Lauder W. Jones and Dr. James F. Norris as Associate Editors.

ARTHUR B. LAMB, *Editor*.

### Report of the Editor of Chemical Abstracts for the Year 1920.

The 1920 volume of *Chemical Abstracts* contains 18,051 abstracts, an increase of 3,353 over the preceding volume. These cover 3,826 pages. The edition has been 15,000 copies per number throughout most of the year. Of the abstracts 13,619 are of journal and like papers and 4,432 of patents. The abstracts of patents have averaged 0.105 page in length and the others 0.223 page, as against 0.115 and 0.244, respectively, in 1919. The reduction in length of abstracts was brought about during the second half of the year owing to budget restrictions. Advances in paper and printing costs, while the amount of literature to be abstracted was increasing rather rapidly, made retrenchment necessary. For this same reason the table of contents and the author indexes to the individual numbers were omitted during the second half of the year. It seemed better to omit something of temporary value only than to hold out abstracts or reduce them further.

By the death, on January 19th, 1919, of Mr. A. Hugh Bryan, who had been Assistant Editor in charge of the section on Sugar, Starch and Gums for almost nine years, we lost a good and faithful worker. His interest in *Chemical Abstracts* never lagged during his long service on the journal.

During the year the plan of the first formula index to *Chemical Abstracts* has been worked out and the compilation has been in progress. Such an index is not easy to prepare. The inclusion of this formula index had added several weeks to the time required to issue the Index Number, but it is believed that its usefulness will make up many times for the

expense and wait involved. A discussion of this index will be found in a foreword at its beginning.

The book title service of *Chemical Abstracts* has been improved. The number of titles published during the year is 1,275. References to published reviews are now given whenever possible.

A coöperative arrangement was made with Mr. Homer F. Staley, Editor of the *Journal of the American Ceramic Society*, during the latter part of the year for the obtaining of abstracts of papers in which both this JOURNAL and *Chemical Abstracts* are interested. The coöperative arrangement with the editors of the *Journal of the Chemical Society (London)* and the *Journal of the Society of Chemical Industry*, entered into in 1919, has worked out very satisfactorily.

A questionnaire sent out last September covering several points in connection with *Chemical Abstracts* contained a request for opinions as to whether five years or ten years would be considered the most suitable period to be covered by the next collective index to the journal. The vote received was 113 for a ten-year and 30 for a five-year index. The opinion seemed to be that a longer span of years per collective index and fewer such indexes would be more satisfactory in the long run in view of the probable usefulness of *Chemical Abstracts* over a long period of years.

At the beginning of 1920 the title of Section 16 was changed from "Fermented and Distilled Liquors" to "The Fermentation Industries." Dr. H. S. Paine assumed charge of this section at that time.

Other new assistant editors are Dr. R. S. Williams, in charge of Metallography, and Dr. F. W. Zerban, in charge of Sugar, Starch and Gums. The value of the journal of the spirit of service shown continually by the assistant editors and abstractors is very great. The editor wishes again to express his appreciation of this spirit and to state his belief that the members of the Society appreciate it.

Statistics for the various sections follow:

	No. pages.	No. abstracts.
Apparatus.....	37.7	250
General and Physical Chemistry.....	243.6	1169
Subatomic Phenomena and Radiochemistry.....	137.1	655
Electrochemistry.....	81.1	368
Photography.....	8.8	48
Inorganic Chemistry.....	61.7	199
Analytical Chemistry.....	137.9	547
Mineralogical and Geological Chemistry.....	68.7	423
Metallurgy and Metallography.....	140.6	640
Organic Chemistry.....	563.2	1016
Biological Chemistry.....	613.7	3138
Foods.....	88.9	580
Water, Sewage and Sanitation.....	50.8	387
Soils, Fertilizers and Agricultural Poisons.....	71.4	377
Fermentation Industries.....	21.7	123

	No. pages.	No. abstracts.
Pharmaceutical Chemistry.....	77.5	450
Acids, Alkalies, Salts and Sundries.....	56.5	375
Glass and Ceramics.....	66.4	298
Cement and Other Building Materials.....	28.9	154
Fuels, Gas, Tar and Coke.....	134.3	583
Petroleum, Asphalt and Wood Products.....	34.5	177
Cellulose and Paper.....	33.4	230
Explosives and Explosions.....	47.6	174
Dyes and Textile Chemistry.....	38.0	219
Paints, Varnishes and Resins.....	36.8	212
Fats, Fatty Oils and Soaps.....	54.9	308
Sugar, Starch and Gums.....	45.3	253
Leather and Glue.....	35.4	132
Rubber and Allied Substances.....	22.1	134
Total not including patents.....	3038.5	13,619
Patent abstracts.....	477.3	4,432
	3515.8	18,051
Book titles.....	66.0	1,275
Headings, blanks and cross references.....	244.2	

3826.0

Respectfully submitted,

E. J. CRANE.

### Report of the Editor of the Journal of Industrial and Engineering Chemistry.

Two prominent features stand out in connection with the *Journal of Industrial and Engineering Chemistry* for the year 1920:

1. As the result of a direct appeal to contributors and of the thorough work of the reviewers in recommending condensations of articles, it has been possible to proceed rapidly with the publication of a large number of articles, thereby enabling at the present time prompt publication of original papers, as far as this is consistent with their thorough review. It is a pleasure here to make grateful acknowledgment of the helpful coöperation of every member of the Society who has been requested to aid in this important work of review of papers.

Throughout the past year we have had the good fortune to have the work of editing papers entirely in charge of Miss Ruth Thomas, formerly of the Research Staff of the Massachusetts Institute of Technology. The painstaking and thorough work of Miss Thomas in preparing the manuscripts for the printer has resulted in a distinct improvement in many papers published during the year. Her valuable work is attested by many of our contributors.

2. On the authorization of the Directors, a complete change in the management of the Advertising Department has been made. This entire matter has been turned over to the Chemical Catalog Company, Inc., on a commission basis, the Society reserving, however, the right of rejection of any advertisement and continuing to develop in consultation with the Chemical Catalog Company the advertising policies of the Journal. The effective work of the new Advertising Department, begun as it was under rather complicated conditions and in the face of a fifty per cent. increase in advertising rates, justifies the hope that during the coming year this feature of the work will be thoroughly taken care of.

On account of the very large increase in rental demanded by the new owners of the former quarters of the Journal, a change of location was made necessary, and it was extremely fortunate that the present admirable rooms could be found in the tower of the Metropolitan Building, where the Advertising Department was already located.

During the year two important new features were added to the Journal, namely, monthly letters from distinguished correspondents in London and Paris. It is hoped to continue to expand this foreign news feature by the inclusion from time to time of occasional letters from other European chemical centers.

As a result of the action of the Directors at the last annual meeting, we have been able to add to our staff in part-time capacity Dr. Robert P. Fischelis, whose experience and interest in publication matters will prove a valuable asset in the work during the coming year.

The A. C. S. New Service continues to grow in usefulness. More and more it is finding a definite and acceptable place in the newspaper offices of the country and under the increased appropriation recently granted, it is proposed to extend this work as far as possible into the field of the weekly newspapers, thereby increasing more and more the public understanding of the significance of chemistry to the nation.

Much time has been required to get the monthly Clip Sheet issued by the News Service thoroughly established. The first attempts to include in this Clip Sheet textually reproduced sections of the Journal did not yield very great success. This was then modified in form to cover popular treatment of articles appearing each month in the Journal, and the clippings being received show that this feature is now on a thorough basis and is being widely made use of by the press.

For comparison with the previous year, there follows a statistical résumé of the contents of the Journal for 1919 and 1920:



	Number of pages.	
	1919.	1920.
Title and Contents.....	12.0	12.0
Editorials.....	37.7	29.0
Chemical Warfare Service.....	166.5	24.9
Other War Activities.....	12.4	....
Original Papers.....	311.1	582.0
Laboratory and Plant.....	81.2	131.2
Features.....	133.6	122.0
Addresses and Contributed Articles.....	82.6	54.8
Symposia.....	39.1	...
Medal Awards.....	7.5	29.7
Works and Laboratory accidents.....	5.4	...
Foreign Industrial News.....	28.7	5.1
Scientific Societies.....	57.5	47.4
Obituaries.....	1.5	2.6
Bibliographies.....	17.2	...
Notes and Correspondence.....	42.9	35.0
Washington Letters.....	18.0	14.1
London Letters.....	...	2.0
Paris Letters.....	...	3.0
Industrial Notes.....	30.0	16.2
Personal Notes.....	22.6	17.4
Government Publications.....	45.1	48.7
Book Reviews.....	15.1	16.9
New Publications.....	12.3	12.0
Market Report.....	12.0	23.0
Index.....	20.0	18.0

Total Editorial Pages..... 1,212.0      1,247.0

Total Advertising Pages..... 1,300      1,312

Total Number of Copies Issued..... 172,600      198,300

Respectfully submitted,

CHAS. H. HERTY, *Editor*.

## COUNCIL.

MEMBERS ELECTED BETWEEN DECEMBER 15, 1920, AND JANUARY 15, 1921.

Adams, C. Calvin, L. H. Gilmer Co., Keystone and Vincent Sts., Tacony, Philadelphia, Pa.

Adan, Robert, 4 Korte Meir, Ghent, Belgium.

Ahlbeck, Harry W., 2229 Harrison St., Evanston, Ill.

Anderegg, L. T., Box 37, Station A., Ames, Iowa.

Anderson, Paul J., 18 Ridge St., S. Manchester, Conn.

Andrews, Fred. R., 1210 Joseph St., New Orleans, La.

Arentz, Fred B., c/o U. S. Industrial Alcohol Co., Res. Lab., S. Baltimore, Md.

Bailey, Douglas P., 1409 E. 2nd St., Austin, Tex.

Baird, Kenneth E., Donner Union Coke Corp., Buffalo, N. Y.

Baird, W. H., Northern Sugar Corp., Mason City, Ia.

Balch, Royal T., 332 Seaton Place, N. E., Washington, D. C.

- Bardwell, Dwight C., 2141 Berkeley Way, Berkeley, Cal.  
 Barker, Wm. F., 143 Duke St., Southport, England.  
 Bass, L. W., 1248 Yale Station, New Haven, Conn.  
 Beckman, Arnold O., 412 E. Green St., Champaign, Ill.  
 Beisel, Harold D., 5067 Spalding Ave., St. Louis, Mo.  
 Benedict, A. J., 328 Seneca Parkway, Rochester, N. Y.  
 Beneke, Walter, 3734 Utah Place, St. Louis, Mo.  
 Bennett, Albert L., 409 Tabor Opera House Bldg., Denver, Colo.  
 Bick, Jacob A., 1076 Roosevelt Road, W., Chicago, Ill.  
 Bishop, Oakley M., 910 Blackshire Road, Wilmington, Del.  
 Bitterman, Grace V., 1717 Chadbourne Ave., Madison, Wis.  
 Blair, J. S., 3409 34th Place, N. W., Washington, D. C.  
 Blakey, Walter, 569 London Road, Oakhill, Stoke-on-Trent, England.  
 Blume, Wm. R., 1269 Madison Ave., New York City.  
 Bluthardt, Oscar D., 412 E. Green St., Champaign, Ill.  
 Bond, James D., 853 Convention St., Baton Rouge, La.  
 Boos, Andrew V., 261 Ryerson St., Brooklyn, N. Y.  
 Boykin, William A., Jr., Ruxton, Md.  
 Brakefield, J. L., Box 526, Baylor University, Waco, Tex.  
 Brash, Lionel V., 1294 Emura St., Honolulu, H. T.  
 Brazil, Ernest, Bauxite, Ark.  
 Bridge, Russell J., 605 Irving Ave., Syracuse, N. Y.  
 Bridgeford, Frank R., 375 N. Michigan Ave., Pasadena, Cal.  
 Brodie, George H., 6 Clarke St., Burlington, Vt.  
 Brody, Samuel, Dairy Bldg., Univ. of Mo., Columbia, Mo.  
 Buck, Raymond, 703 Stanton Ave., Springfield, O.  
 Butler, Joseph, c/o Syracuse Lighting Co., Gas Dept., 143 Mechanic St., Syracuse, N. Y.  
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[Full accounts of all meetings should be sent to Secretary Charles L. Parsons,  
 1709 G St., N. W., Washington, D. C.]

#### CHICAGO SECTION.

A joint meeting of the Chicago Section of the American Chemical Society and the American Association for the Advancement of Science was held in Chicago on December 29. Two addresses were made, as follows: "Some Present Aspects of Chemistry in the United States," by B. F. Lovelace, of Johns Hopkins University; and "Experimental Tests of the Radiation Hypothesis," by Farrington Daniels, of the University of Wisconsin.

S. L. REDMAN, *Secretary*.

#### CLEVELAND SECTION.

On December 21, H. N. Holmes, of Oberlin College, addressed the Section on "Applications of Colloidal Chemistry." Attendance, 30%.

H. S. BOOTH, *Secretary*.

## DETROIT SECTION.

The 121st meeting of the Section occurred on December 15, the address of the evening being given by A. F. MacFarland, of the Vanadium-Alloy Steel Co., who spoke on "The Relation Between Chemical Analyses and the Quality of Tool Steels."

WM. B. TEMPLETON, *Secretary*.

## INDIANA SECTION.

At the regular meeting of the Section, held on January 14, the following program was given: "Activated Nitrogen, Hydrogen, and Oxygen," by F. O. Anderegg, of Purdue University; and "A Movement to Establish the Coöperative Relation Between Science and the Industries in Indiana," by I. H. Derby, of the Republic Creosoting Company.

EDGAR B. CARTER, *Secretary*.

## KANSAS CITY SECTION.

The 147th meeting of the Kansas City Section was held on December 11. Two addresses were given, as follows: "History of the Kansas City Section," by F. B. Dains; and "Chemical Control of Bread-Making," by C. J. Patterson. The following officers were elected for 1921: H. C. Allen, *Chairman*; W. B. Smith, *Vice-Chairman*; Lee Clark, *Secretary-Treasurer*; H. M. Elsey, *Assistant Secretary*; F. B. Dains and Rudolph Hirsch, *Councilors*. Attendance, 23%.

W. B. SMITH, *Secretary*.

## LEHIGH VALLEY SECTION.

The following officers have been elected by the Section for the year 1921: Henry J. Wysor, *Chairman*, and Judson G. Smull, *Secretary-Treasurer*.

JUDSON G. SMULL, *Secretary*.

## LOUISVILLE SECTION.

The first fall meeting of the Section was held on November 5, when the following officers were elected for 1921: G. A. Goodell, *Chairman*; C. E. Geiger, Jr., *Secretary*; and Alfred W. Homberger, *Councilor*.

C. E. GEIGER, JR., *Secretary*.

## MICHIGAN AGRICULTURAL COLLEGE SECTION.

The following officers were elected by the Section for the year 1921: R. C. Huston, *Chairman*; D. L. Dandall, *Vice-Chairman*; C. S. Robinson, *Secretary*; O. B. Winter, *Treasurer*; and A. J. Patten, *Councilor*.

C. S. ROBINSON, *Secretary*.

## MIDLAND SECTION.

At a meeting of the Section, held on December 8, Thomas Griswold, Jr., presented a paper entitled, "Reminiscences." Attendance, 66 $\frac{2}{3}$ %.

C. C. KENNEDY, *Secretary*.

## MILWAUKEE SECTION.

On September 3, Arthur Thomas spoke before the Section on the subject, "Physical Chemistry."

D. M. Buck, of the American Sheet and Tin Plate Co., gave an illus-

trated lecture, September 24, before the Section on the manufacture of tin plate.

At a business meeting held on October 15, the following officers were elected for the year: C. A. Nash, *Chairman*; C. N. Davidson, *Vice-Chairman*; W. H. Kloppenburg, *Secretary*; E. J. Kern, *Treasurer*; J. A. Wilson and G. N. Prentiss, *Councilors*.

On January 14, Edwin J. Kern, *Treasurer* of the Section, spoke before the regular meeting on the subject, "The Estimation of Tannin."

WM. H. KLOPPENBURG, *Secretary*.

#### MINNESOTA SECTION.

At the 90th meeting of the Section, held on December 3, Julius Stieglitz, of the University of Chicago, spoke on "The Theory of Color Production." Attendance, 350.

On January 6, J. F. McClendon, of the School of Medicine, University of Minnesota, addressed the Section on "The Chemical Basis of Education."

L. M. HENDERSON, *Secretary*.

#### NEBRASKA SECTION.

The Section has elected the following officers for 1921: Ernest Anderson, *Chairman*; W. S. Frisbie, *Vice-Chairman*; S. B. Arenson, *Secretary-Treasurer*; F. W. Upson, *Councilor*; H. G. Deming, H. A. Durham, and D. J. Brown, *Executive Committee*. Attendance at December 14th meeting, 50%.

B. CLIFFORD HENDRICKS, *Secretary*.

#### NEW YORK SECTION.

The program for the regular meeting held on January 7 was as follows: "New Points of Contact Between University and Industry," by Warren K. Lewis, and "Heat Factors of Oil Shale Distillation," by R. H. McKee and E. E. Lyder.

HERBERT G. SIDDEHOTTOM, *Secretary*.

#### NORTHEASTERN SECTION.

The 163rd regular meeting of the Section occurred on January 14, when Jaques Bronfenbrenner, assistant professor of Preventive Medicine and Hygiene at the Medical School of Harvard University, spoke on "Some Chemical Problems in Bacteriology," illustrated by lantern slides.

L. F. HAMILTON, *Secretary*.

#### OMAHA SECTION.

At the 3rd meeting of the Section, held on October 19, papers were presented as follows: "The Dynamics of Catalase Action," by A. Morgulis; and "Some Observations on Corrosion in Boilers," by W. M. Barr.

The 4th meeting was held on November 16, at which time Gerald Wendt, of the University of Chicago, addressed the Section of "Electrometric Filtration."

On December 14, John T. Myers presented a paper before the members of the Section, his subject being, "Sulfur Producing Bacteria."

The following officers have been elected by the Section for the year 1921: H. A. Senter, *Chairman*; Dean Yohe, *Vice-Chairman*; E. M. Partridge, *Secretary-Treasurer*; Wm. M. Barr, *Councilor*; C. F. Crowley, J. A. Land and R. W. Savidge, *Executive Committee*.

The 6th meeting of the Section was held at the Creighton Dental College in January, at which time a paper was presented by Wm. G. Haynes on the "Inspection of Oils and Paints."

E. M. PARTRIDGE, *Secretary*.

#### PITTSBURGH SECTION.

At the 167th regular meeting of the Section, on November 18, Duncan MacRae, of the Westinghouse Electric and Manufacturing Co., spoke on "The Manufacture of Incandescent Tungsten Filament Bulbs."

At the 168th regular meeting, held on December 16 at the Mellon Institute, F. C. Binnall, Engineer for the General Oil Gas Corporation of New York City, addressed the members on "The Dayton Oil Gas Process."

On January 20, R. B. Gilmore spoke before the Section on "Some Problems in Graphite Crucible Manufacture."

G. W. JONES, *Secretary*.

#### RHODE ISLAND SECTION.

A joint meeting was held with the Providence Engineering Society on December 21. Ellwood Hendrick spoke on the subject, "Chemistry for Everyman."

On January 21, Norman E. Holt addressed the Section on "The Bucher Process as Utilized by the Ordnance Department During the War."

HERBERT F. DAVISON, *Secretary*.

#### ROCHESTER SECTION.

The 116th meeting of the Section occurred on January 10, at the University of Rochester. William Webb, of the Eastman Kodak Company, spoke on "Camphor, Natural and Synthetic."

ERLE M. BILLINGS, *Secretary*.

#### SAVANNAH SECTION.

The regular monthly meeting of the Section was held on December 16, when the following papers were presented: "The Economic Loss from Principal Causes of Death in Savannah with Special Reference to Malaria," by Alfred Larsen; "The Economic Loss from Syphilis, with Some Remarks on the Methods of Diagnosis of the Disease," by V. H. Bassett; and "The Wassermann Complement Fixation test for Syphilis," by Daniel Secklinger. All papers were illustrated by charts and pictures.

At this meeting the following officers for 1921 were elected: Herbert S. Bailey, *Chairman*; Joseph Callaway, Jr., *Vice-Chairman*; Herbert P. Stack, *Secretary-Treasurer*; and F. N. Smalley, *Councilor*. Attendance, 38%.

HERBERT P. STACK, *Secretary*.

## SOUTHEAST TEXAS SECTION.

The following officers for 1921 have been elected by the Section: H. B. Weiser, *Chairman*; L. S. Bushnell, *Vice-Chairman*; P. S. Tilson, *Secretary*; L. S. Howell, *Treasurer*; F. W. Bushong, *Councilor*.

P. S. TILSON, *Secretary*.

## ST. LOUIS SECTION.

At the regular December meeting, the Section elected the following officers for 1921: F. W. Russe, *Chairman*; L. F. Nickell, *Vice-Chairman*; H. A. Carlton, *Secretary*; O. H. Pierce, *Treasurer*; L. McMaster and P. A. Shaffer, *Councilors*.

L. G. Blakeslee read a paper on "The Bearing of Some of the Federal Laws on the Chemical Business," before the regular meeting of the Section, January 3.

H. A. CARLTON, *Secretary*.

## SYRACUSE SECTION.

The first extra winter meeting of the Section was held on January 7, when C. G. Derick addressed the members on "Methods of Attacking a Research Problem." Attendance,  $33\frac{1}{8}\%$ .

BYRON W. GRIMES, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

At the annual business meeting of the Section, held on December 14, the following officers were elected for 1921: A. H. White, *Chairman*; C. C. Meloche, *Secretary-Treasurer*; H. H. Willard, *Councilor*; C. S. Schoepfle, F. E. Bartell, W. L. Badger, *Executive Committee*. Attendance, 40%.

R. J. CARNEY, *Secretary*.

## UNIVERSITY OF MISSOURI SECTION.

The annual meeting of the Section was held on December 17, when the following papers were presented: "Coumarin Extraction," by R. M. Smith; and "Carbon Determinations in Plant Tissues," by T. E. Friedemann. Officers for the year 1921 were elected, as follows: S. Calvert, *Chairman*; W. J. Robbins, *Vice-Chairman*; H. D. Hooker, Jr., *Secretary*; L. D. Haigh, *Treasurer*; and C. R. Moulton, *Treasurer*.

HENRY D. HOOKER, JR., *Secretary*.

## VIRGINIA SECTION.

The 39th meeting of the Section was held on January 21, when E. C. L. Miller spoke on "Hydrogen-Ion Concentration and its Determination." Following the lecture, moving pictures pertaining to chemistry, loaned by the Bureau of Commercial Economics, were exhibited. Attendance at December meeting, 28%.

ROBT. F. MCCracken, *Secretary*.

## WASHINGTON, D. C., SECTION.

The 313th meeting of the Section was held at the Cosmos Club. The address of the evening was delivered by R. C. Tolman, director of the Nitrogen Fixation Laboratory, Ordnance Bureau, War Department, his subject being "The Third Law of Thermodynamics."

J. B. REED, *Secretary*.

# Proceedings.

## COUNCIL.

Dr. E. F. Smith, President of the American Chemical Society, has changed the name of the Committee on Institute for Drug Research to the Committee on Institute for Chemo-Medical Research, and has appointed Dr. C. L. Alsberg, of Washington, D. C., to fill the vacancy on the Committee created by the resignation of Dr. P. A. Levene.

## Auditors' Report.

New York, January 28, 1921.

DR. J. E. TEEPLE, *Chairman Finance Committee*,  
American Chemical Society,  
50 East 41st Street, New York City.

DEAR SIR:

Pursuant to your request, we have made an audit of the books of account of the American Chemical Society, kept by its Treasurer, for the year ending December 31, 1920, and submit herewith the accompanying Condensed General Balance Sheet as of December 31, 1920, and Statement of Cash Received and Disbursed between January 1, and December 31, 1920—marked Exhibit "A" and Exhibit "B," respectively, which we have prepared therefrom; and hereby

CERTIFY that such statements correctly reflect the financial condition of the Society at December 31, 1920 and its financial transactions during the year, as shown by the books of account.

Yours very truly,

MCCULLOH AND BROWN,  
*Certified Public Accountants.*

## AMERICAN CHEMICAL SOCIETY.

### CONDENSED GENERAL BALANCE SHEET—DECEMBER 31, 1920.

#### ASSETS.

#### INVESTMENTS:

Special investment fund:		Market value.	
\$1,000 Brooklyn Rapid Transit 7% Notes, Due July 1, 1922.....	\$	400.00	\$ 1,000.00
1,000 Hocking Valley Railway 1st Mortgage 4½%, Due July 1, 1999..		690.00	1,000.00
6,000 Illinois Central-Chicago, St. Louis and New Orleans Joint 1st Re- funding Mortgage 5%, Due December 1, 1963.....		4,792.50	6,000.00
1,000 Northern Pacific Great Northern- Chicago, Burlington and Quincy 4%, Due July 1, 1921.....		960.00	1,000.00

1,000 New York Connecting Railway 1st Mortgage 4 <sup>1</sup> / <sub>2</sub> %, Due August 1, 1953.....	755.00	1,000.00
2,000 Atlas Portland Cement 6%, Due March 1, 1925.....	1,760.00	2,000.00
2,000 Corporate Stock City of New York 4 <sup>1</sup> / <sub>2</sub> %, Due June 1, 1965.....	1,840.00	2,000.00
5,000 New York Central Refunding & Improvement 4 <sup>1</sup> / <sub>2</sub> %, Series "A," Due October 1, 2013.....	3,700.00	5,000.00
10,000 United States Steel Corporation 5%, Due April 1, 1963.....	9,300.00	10,000.00
15,000 United States Liberty 2nd 4 <sup>1</sup> / <sub>4</sub> %, Due 1942.....	12,765.00	14,608.00
20,000 United States Liberty 3rd 4 <sup>1</sup> / <sub>4</sub> %, Due 1928.....	17,596.00	19,400.00
15,000 United States Liberty 4th 4 <sup>1</sup> / <sub>4</sub> %, Due 1933-1938.....	12,780.00	14,604.00
10,000 United States Victory 4 <sup>3</sup> / <sub>4</sub> %, Due 1922-1923.....	9,600.00	10,000.00
10,000 New York Telephone Company 6%, Due February 1, 1949.....	8,700.00	9,987.50
10,000 United Kingdom of Great Britain and Ireland 5 <sup>1</sup> / <sub>2</sub> %, Due February 1, 1937.....	8,300.00	9,875.00
10 Shares Chemical Foundation Inc. Stock—(Subscription Receipt Central Union Trust Company.	1,000.00	1,000.00
Total.....	\$ 94,938.50	\$108,474.50

## Life Membership Fund:

\$1,000 United States Liberty, 2nd 4 <sup>1</sup> / <sub>4</sub> %, Due 1942.....	\$ 851.00	\$ 908.75
1,000 United States Liberty, 4th 4 <sup>1</sup> / <sub>4</sub> %, Due 1933-1938.....	852.00	906.95
1,000 Corporate Stock City of New York 3 <sup>1</sup> / <sub>2</sub> %, Due November 1, 1928...	890.00	1,000.00
2,000 Mutual Union Telegraph 5%, Due May 1, 1941.....	1,520.00	2,000.00

Total.....	\$ 4,113.00	4,813.70
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## Morris Loeb Fund:

\$6,000 United States Liberty, 4th 4 <sup>1</sup> / <sub>4</sub> %, Due 1933-1938.....	\$ 5,112.00	\$ 5,100.90
5,000 Hocking Valley Railway 1st Mortgage 4 <sup>1</sup> / <sub>2</sub> %, Due July 1, 1999...	3,450.00	5,000.00
5,000 Illinois Central-Chicago, St. Louis and New Orleans Joint 1st Refunding Mortgage 5%, Due December 1, 1963.....	3,993.75	5,000.00



5,000 New York Connecting Railway 1st Mortgage 4½%, Due August 1, 1953.....	3,775.00	5,000.00
5,000 Northern Pacific Great Northern- Chicago, Burlington and Quincy 4%, Due July 1, 1921.....	4,800.00	5,000.00
Total.....	\$ 21,130.75	25,100.90
Total Investments.....	\$120,182.25	\$138,389.10
OFFICE FURNITURE AND FIXTURES.....		4,772.71
PUBLICATIONS (Extra Copies Held for Future Sale).....		8,000.00
CURRENT ASSETS:		
Cash in Bank and on Hand—As per Exhibit "B".....	\$ 1,526.39	
Accounts Receivable—Advertising.....	19,405.02	
Total.....		20,931.41
TOTAL ASSETS.....		\$172,093.22

## LIABILITIES.

## TRUST FUNDS AND UNEXPENDED CASH BALANCE:

Morris Loeb Trust Fund.....	\$25,100.90
Life Membership Fund.....	5,411.55
Life Membership Income—Dues and Interest.....	464.52
Total.....	\$ 30,976.97
BALANCE—BEING EXCESS OF ASSETS OVER LIABILITIES.....	141,116.25

TOTAL LIABILITIES..... \$172,093.22

THIS IS TO CERTIFY that we have audited the records and books of account of the American Chemical Society, kept by its Treasurer, and have prepared therefrom the foregoing Balance Sheet, which correctly reflects the financial condition of the Society as at December 31, 1920, as shown by its books of account.

The securities were confirmed by actual count, and the cash proven by certificate from the depository.

McCULLOH AND BROWN,  
*Certified Public Accountants.*

## AMERICAN CHEMICAL SOCIETY.

## STATEMENT OF CASH RECEIVED AND DISBURSED BETWEEN JANUARY 1, AND DECEMBER 31, 1920.

## RECEIPTS.

CASH ON HAND JANUARY 1, 1920.....	\$ 27,281.00
DUES AND SUBSCRIPTIONS:	
Membership Dues and Subscriptions.....	\$140,482.00
Life Membership Dues.....	1,050.00
Total.....	141,532.00

## MISCELLANEOUS:

Cancellation of Office Lease—Industrial Journal.....	\$ 2,800.00
Desk Room Rent—Secretary's Office.....	262.50

Notes Payable—Discounted.....	19,000.00
Bank Acceptances—Payment at Maturity Excluding Interest Realized Therefrom.....	86,688.77
Secretary's Remittances—Applicable to the Year 1921...	35,000.00

Total..... 143,751.27

REVENUE FROM PUBLICATIONS:

Advertising.....	\$ 71,906.65
Non-Members Subscriptions.....	15,863.98
Back Numbers.....	9,127.02
Directories.....	18.00
Reprints (Secretary's Office).....	1,626.81

Total..... 98,542.46

DECENNIAL INDEX:

Subscriptions and Contributions.....	1,699.00
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INCOME FROM INVESTMENTS, ETC.:

Special Investment Fund.....	\$ 5,114.98
Bank Acceptances.....	1,314.92
Life Membership Fund.....	198.48
Morris Loeb Trust Fund.....	1,092.11
General Funds—Interest on Bank Balances.....	1,069.22

Total..... 8,789.71

PREPAYMENT OF EXPENSES, ETC.:

Payments by Members for Postage.....	\$ 3,709.05
Miscellaneous Items.....	26.41

Total..... 3,735.46

TOTAL RECEIPTS..... \$425,330.90

DISBURSEMENTS.

INVESTMENTS AND CAPITAL EXPENDITURES:

Securities Purchased:

United States Liberty Bonds, 2nd & 4th 4 $\frac{1}{4}$ % (Life Membership Fund).....	\$ 1,813.70
United States Liberty Bonds, 4th 4 $\frac{1}{4}$ % (Morris Loeb Fund).....	5,100.90
Bank Acceptances.....	86,688.77

Total..... \$ 93,603.37

TEMPORARY LOANS—NOTES DISCOUNTED PAID..... 19,000.00

INTEREST PAYMENT TO SMITHSONIAN INSTITUTE FROM MORRIS LOEB FUND INCOME..... 2,007.24

PUBLICATION EXPENSES:

*Journal:*

Editor's Salary.....	\$ 1,000.00
Clerical Salaries.....	1,033.04
Expenses.....	499.23
Printing Reading Matter.....	41,390.64

Printing Advertisements.....	1,206.40		
Printing Reprints.....	1,318.49		
			\$ 46,447.80
<i>Chemical Abstracts:</i>			
Editor's Salary.....	\$ 4,000.00		
Associate Editor's Salary.....	2,500.00		
Assistant Editor's Salaries.....	760.64		
Abstractors.....	6,983.20		
Clerical Salaries.....	4,217.34		
Expenses.....	1,124.71		
Printing Reading Matter.....	61,920.92		
Printing Advertisements.....	1,764.16		
Formula Index.....	514.90		
			83,785.87
<i>Journal of Industrial and Engineering Chemistry:</i>			
Editor's Salary.....	\$ 7,500.00		
Assistant Editor's Salary.....	2,500.00		
Staff Correspondents.....	2,424.63		
Clerical.....	6,869.90		
Expenses.....	3,258.21		
Office Rent.....	4,447.22		
Printing Reading Matter.....	41,473.15		
Printing Advertisements.....	33,810.24		
Printing Reprints.....	2,183.24		
			104,466.59
<i>Advertising Department:</i>			
Salaries and Commissions.....	\$ 5,378.81		
Expenses and Rent.....	1,047.07		
Printing Reprints and Cuts.....	93.99		6,519.87
FORWARD.....		\$241,220.13	\$114,610.61
PUBLICATION EXPENSES (Forward).....		\$241,220.13	
<i>News Service:</i>			
Director's Salary.....	\$ 2,800.00		
Clerical Salaries.....	1,500.00		
Office Rent.....	726.68		
Expenses.....	3,052.01		
			8,078.69
Back Numbers.....			3,635.47
Total.....			252,934.29
LOCAL SECTIONS.....			7,671.55
<i>SECRETARY'S OFFICE:</i>			
Secretary's Salary.....	\$ 5,000.00		
Clerical Salaries.....	9,235.00		
Office Rent.....	1,359.00		
Expenses.....	4,633.40		
Total.....			20,227.40

## TREASURER'S OFFICE:

Treasurer's Salary.....	\$ 1,000.00
Clerical Salaries.....	960.00
Expenses.....	1,080.30

Total..... 3,040.30

PRESIDENT'S OFFICE..... 348.98

EXPENDITURES FOR 1919 FROM 1920 RECEIPTS..... 20,000.00

## GENERAL EXPENSES, ETC.:

General Meetings.....	\$ 1,703.48
Life Membership Dues.....	170.00
International Tables of Physical and Chemical Constants	300.00

## Monographs:

Editors' Salaries.....	\$ 2,000.00
Expenses.....	151.14

2,151.14

Interest on Borrowed Capital..... 77.50

Incidentals..... 569.26

Total..... 4,971.38

TOTAL DISBURSEMENTS..... \$423,804.51

BALANCE—CASH ON HAND DECEMBER 31, 1920..... 1,526.39

TOTAL..... \$425,330.90

## Report of the Treasurer.

New York City, N. Y., February 10, 1921.

The preceding report of the Auditors gives the Balance Sheet of your Society as of December 31, 1920 and the total receipts and disbursements for the year 1920.

In examining the Balance Sheet we should remember that the Morris Loeb Fund and the income from it does not belong in any way whatever to the American Chemical Society. We are simply the trustees of this Fund and hand over all the income to the Smithsonian Institution for maintaining the Morris Loeb Museum. In the same way we should remember that the Life Membership Fund does not belong to the American Chemical Society for any purpose whatever excepting for furthering research work if that should be undertaken at any time, and that the income from this Fund does not belong to the Society excepting for paying the dues of living life members. We are simply the custodian of these two Funds and cannot use them or their income in any way for the general purposes of the Society. The Special Investment Fund represents our real surplus. You will note that this has not been changed in any way during the year either by purchase or sale. Its market value as indicated, is less than it was a year ago simply on account of the depreciation in value of all securities. The Office Furniture and Fixtures, and Publica-

tions are carried at the same figures as they were a year ago. We have no liabilities excepting our liability for the proper handling of our Trust Funds, consequently our situation at the end of the year 1920 and at the end of the year 1919 may be easily compared by comparing our current assets.

At the end of 1919 our cash assets were \$27,281.00. From this, however, we must deduct \$6,016.03 income from the Morris Loeb Fund which was included in this cash item, and \$1,807.59 income from the Life Membership Fund—a total of \$7,823.62. We must also deduct \$20,000 which we had already used out of 1920 funds. This left a cash deficit of \$542.62.

At the end of 1920 we had cash on hand of \$1,526.39, from which must be deducted \$464.52 Life Membership Income, and from which must further be deducted \$35,000 which we had used out of 1921 funds, leaving a cash deficit December 31, 1920 of \$33,938.13.

A comparison of the figures for the two years, then, shows that our cash position at the end of 1920 was \$33,395.51 worse than it was twelve months previously, and the only offset to this is that our Accounts Receivable from advertising had increased about \$10,000 during the year.

If we now take the question of Receipts and Disbursements and eliminate all Trust items, all short term transactions which were begun and concluded during the year, we get a net operating account of the Society's activities for the year 1920 as follows:

#### RECEIPTS.

Membership Subscriptions.....	\$140,482.00
Subscriptions, non-members.....	15,863.98
Back Numbers, net.....	5,491.55
Directories.....	18.00
Reprints.....	1,626.81
Decennial Index.....	1,699.00
Postage.....	3,735.46
Advertising, net.....	28,605.98
Interest.....	7,499.12
<b>TOTAL.....</b>	<b>\$205,021.90</b>

#### DISBURSEMENTS.

##### *Journal:*

Salaries.....	\$2,083.04
Expenses.....	499.23
Printing.....	42,709.13
	<hr/>
	\$ 45,291.40

##### *Chemical Abstracts:*

Salaries.....	18,461.18
Expenses.....	1,124.71
Printing.....	62,435.82
	<hr/>
	82,021.71

*Industrial Journal:*

Salaries.....	19,294.53	
Expenses.....	4,905.43	
Printing.....	43,656.39	
		<hr/>
		67,856.35
News Service.....		8,078.69
Local Sections.....		7,671.55
Secretary's Office, net.....		19,964.90
Treasurer's Office.....		3,040.30
President's Office.....		348.98
General Meetings.....		1,703.48
Monographs.....		2,151.14
Miscellaneous.....		946.76
Total.....		\$239,025.26
Deduct Receipts.....		205,021.90

Net Operating Deficit..... \$ 34,003.36

In our Finance Committee's report of September 2, 1920, which was presented at the Chicago Meeting, we estimated that this deficit would be \$27,000 if no further increases in printing occurred, but increases in cost of printing did occur, resulting in the \$34,000 deficit for the year. Hence the increase in dues to \$15.00.

If we assume that the membership dues received represented 14,000 paying members, our Receipts and Disbursements per year are distributed as follows:

## RECEIPTS.

Dues.....	\$10.00
Advertising, net.....	2.04
Other income.....	2.57
	<hr/>
Total.....	\$14.61

## DISBURSEMENTS.

Journal.....	\$ 3.23
Abstracts.....	5.84
Industrial Journal.....	4.84
News Service.....	0.57
Local Sections.....	0.55
Secretary's Office.....	1.43
Treasurer's Office.....	0.22
President's Office.....	0.02
General Meetings.....	0.12
Monographs.....	0.15
Miscellaneous.....	0.07

Total..... \$17.04

leaving a net deficit of \$2.43 per member, and indicating that each member, for his \$10.00 dues, received \$17.04 either in Society Journals or Society activities.

JOHN E. TREEPLE, *Treasurer.*

## MEMBERS ELECTED BETWEEN JANUARY 15 AND FEBRUARY 15, 1921.

- Abbett, James M., 1106 Colusa Ave., Berkeley, Calif.  
 Abbett, Raymond F., 923 Elberon Ave., Cincinnati, O.  
 Adler, L., 4105 Lafayette Ave., St. Louis, Mo.  
 Alderman, C. Nelson, 33 French St., Fall River, Mass.  
 Allen, Edwin J., 61 Erie Ave., Newton Hlds., Mass.  
 Anderson, E. G., Carnegie Institution, Cold Spring Harbor, L. I., N. Y.  
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#### MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.]

##### AMES SECTION.

On January 13, Fred Upson, head of the Department of Chemistry, University of Nebraska, addressed the Ames Section on "The Life and Researches of J. U. Nef."

H. L. MAXWELL, *Secretary.*

##### CALIFORNIA SECTION.

The 120th regular meeting of the Section occurred on January 28, when the following program was given: "The Chemical Effect of Alpha Particles," by S. C. Lind, physical chemist of the U. S. Bureau of Mines; and "Refining of Zinc by Electrolysis," by Oliver C. Ralston, metallurgist, of the U. S. Bureau of Mines.

LLOYD W. CHAPMAN, *Secretary.*

## CHICAGO SECTION.

On January 21, Paul Nicolas Leech, of the American Medical Association, spoke before the Section on the subject of "Home Remedies." This meeting was designated as Ladies' Night, being the third of a series of meetings given over to topics of interest to members and their wives.

At the regular meeting of the Section, held on February 18, L. V. Redman delivered a lecture on "Phenol Condensation Products." The discovery, development, manufacture and application of phenol condensation products, were covered.

S. L. REDMAN, *Secretary*.

## CINCINNATI SECTION.

The 239th regular meeting of the Section was held in the Chemistry Auditorium of the University of Cincinnati on January 29. The following program was given: "A Simple Method of Determining the Refractive Index of a Liquid by Means of a Microscope," by O. C. Von Schlichten, Geology Department, University of Cincinnati; and "On the Nature of Vegetable Tanning," by G. D. McLaughlin, director of the tanning research department of the University of Cincinnati.

At the 240th regular meeting of the Section, on February 9, C. R. Bragdon, chemical superintendent of the Varnish Works of the Ault & Wiborg Co., spoke on "The Transition Period in Varnish Manufacture."

C. H. LUND, *Secretary*.

## CLEVELAND SECTION.

On January 25, W. Forsythe, of the National Lamp Works, addressed the Section on the subject of "Pyrometers and High Temperature Measurement." Attendance, 60%.

HAROLD S. BOOTH, *Secretary*.

## COLORADO SECTION.

The regular meeting of the Section, held on January 24, in the Denver Public Library, was addressed by H. Mendelson, of the Great Western Sugar Company, on "Chemistry in Agriculture of To-day."

RUTH B. VERTREES, *Secretary*.

## CONNECTICUT VALLEY SECTION.

On January 22, H. S. Miner, of the Welsbach Co., spoke before the Section on "Industrial Lighting."

John S. Shearer, of Cornell University, addressed the members of the Section on February 5, his subject being "Some Recent Applications of X-Rays in the Study of Metals." Attendance, 350.

G. B. HOGABOOM, *Secretary*.

## CORNELL SECTION.

L. B. McMillan, consulting engineer of the Johns-Manville Co., addressed the Section on January 19, his subject being "Heat Insulators."

The regular meeting of the Section occurred on January 25, when John E. Teeple, consulting chemist and chemical engineer, and Treasurer of

the American Chemical Society, spoke on "Chemistry and Engineering in American Potash Manufacture."

F. R. GEORGIA, *Secretary*.

#### DETROIT SECTION.

The 122nd meeting of the Section was held on January 19, when H. P. Kimber of the Pittsburgh Electric Furnace Co., spoke on "Synthetic Iron."

WM. B. TEMPLETON, *Secretary*.

#### EASTERN NEW YORK SECTION.

On January 28, J. C. McLennan, director of the Physical Laboratory at the University of Toronto, addressed the Section on "Helium, Its Production and Uses." Attendance, 61%.

F. K. Richtmeyer, of Cornell University, spoke before the Section, February 18, on "Some Problems of Physiological Optics." Attendance, 46%.

MARY R. ANDREWS, *Secretary*.

#### GEORGIA SECTION.

The regular meeting of the Section occurred on January 19, when E. M. Symmes, of the Hercules Powder Co., gave an address before the members on the subject, "The Manufacture of Dynamite and Gelatin," illustrated by moving pictures.

J. S. BROGDON, *Secretary*.

#### IOWA SECTION.

On February 19, the following program was carried out by the Section at Cedar Rapids, Iowa: "Electromotive Forces and Free Energy of Dilution of Potassium Bromide," by H. B. Hart; "The Adsorption of Dyes by Pleistocene Clays," by J. N. Pearce; "Source of Sodium Chloride in Rain and Snow," by Nicholas Knight; "Animal Utilization of Pentose," by E. W. Rockwood; and "Further Observations of the Migration of Acyl," by J. R. Couture and L. Chas. Raiford.

L. C. RAIFORD, *Secretary*.

#### KANSAS CITY SECTION.

The Kansas City Section held its January meeting on January 22, when the following program was given: "Some Aspects of Chemical Manufacture," by W. H. Leverett, of the National Zinc Company; and "Chemistry of Salvarsan," by Ray Brewster, of the University of Kansas.

On February 9, Wm. H. Walker, of the Massachusetts Institute of Technology, spoke before the members on "Chemistry in the Last War and in the Next." Attendance, 51%.

LEE E. CLARK, *Secretary*.

#### LEXINGTON SECTION.

The 67th meeting of the Section occurred on January 27, when the following papers were read: "Preparation and Selection of Crystals for Measurement," by F. E. Tuttle; and "The Microscopic Examination of Feeding Stuffs and Drugs," by E. J. Jackson.

S. D. AVERITT, *Secretary*.

## LOUISVILLE SECTION.

On January 25, E. M. Symmes, of the Hercules Powder Company, gave a talk before the Section on "The Manufacture of Dynamite and Gelatin."

C. E. GEIGER, JR., *Secretary*.

## MAINE SECTION.

The annual meeting of the Section occurred on January 19, when L. J. Waldbauer spoke on "Moving Picture Films." The following officers were chosen for 1921: C. A. Brautlecht, chairman; J. M. Bartlett, vice-chairman; L. J. Waldbauer, secretary-treasurer; and A. B. Larcher, councilor. Attendance, 30%.

B. F. BRANN, *Secretary*.

## MARYLAND SECTION.

The 47th meeting of the Section was held on January 28. Robert W. Wood, of Johns Hopkins University, spoke on "High Power Fluorescence and Phosphorescence and their Relation to Chemical Change."

C. CLIFTON HOWES, *Secretary*.

## MIDLAND SECTION.

On February 9, Mr. Paul Cottringer, of the Dow Chemical Company, addressed the Section on "The Manufacture of Synthetic Phenol."

C. C. KENNEDY, *Secretary*.

## MILWAUKEE SECTION.

At the meeting of the Section, held on February 18, Carl S. Miner, of Chicago, spoke before the members on "Patents and Their Relation to Chemists and Chemical Industry."

WM. H. KLOPPENBURG, *Secretary*.

## MINNESOTA SECTION.

On February 18, William Moore, of the University of Minnesota, addressed the Section on the subject, "Theory of Adherence of Arsenical Sprays."

L. M. HENDERSON, *Secretary*.

## NASHVILLE SECTION.

The 10th meeting of the Nashville Section was held on January 24. E. M. Symmes spoke to the members on "The Manufacture of Dynamite and Gelatin."

H. A. WEBB, *Secretary*.

## NEBRASKA SECTION.

The 95th meeting of the Section, on January 20, was addressed by W. S. Frisbie, of the Bureau of Foods, Drugs and Oils of the State of Nebraska, his subject being "Some of the Problems of a State Chemist." Attendance, 33 $\frac{1}{3}$ %.

At a special meeting, held on January 22, F. W. Upson and T. J. Thompson reported on substituted alkyl phenyl succinic acids. Attendance, 30%.

On February 24, Victor Lenher, professor of chemistry at the Uni-

versity of Wisconsin, who was a guest of the University of Nebraska and the Local Section, spoke to the members on "Selenium Oxychloride."

S. B. ARNSEN, *Secretary*.

#### NEW HAVEN SECTION.

At the annual meeting of the Section, held on January 28, S. F. Acree, spoke on "The Measurement and Significance of Hydrogen-Ion Concentration in Chemical and Biological Work."

BLAIR SAXTON, *Secretary*.

#### NORHEASTERN SECTION.

The 164th regular meeting of the Northeastern Section was held on February 11, when the following program was given: "The Uses of Silicate of Soda in Industry," by James G. Vail, chemical director of the Philadelphia Quartz Company; and "The Cold Storage of Food in Massachusetts," by Hermann C. Lythgoe, director of the division of food and drugs of the Public Health of the Commonwealth of Massachusetts.

I. F. HAMILTON, *Secretary*.

#### NORTH CAROLINA SECTION.

At a call meeting of the Section, held on January 14 in Raleigh, N. C., the members of the North Carolina Section were addressed by E. M. Symmes, chemical director of the Hercules Powder Co., on the subject of "The Manufacture of Dynamite and Gelatin."

LELAND B. RHODES, *Secretary*.

#### OMAHA SECTION.

The 7th meeting of the Section, on February 8, had as its speaker H. H. Nicholson, mining engineer, formerly head of the Department of Chemistry, University of Nebraska.

E. M. PARTRIDGE, *Secretary*.

#### PHILADELPHIA SECTION.

On January 20, Harrison E. Howe, chairman of the Division of Research Extension, National Research Council, addressed the Section on "The Importance of Organized Science to Chemistry."

At the regular monthly meeting of the Section, held on February 17, Wm. J. Gies, of Columbia University, spoke on "The Dentrifice Problem Viewed from the Standpoint of Recent Chemical Findings." Attendance, 17%.

J. HOWARD GRAHAM, *Secretary*.

#### PITTSBURGH SECTION

The 169th meeting of the Section was held on January 20, when R. B. Gilmore, ceramic engineer for the Vesuvius Crucible Co., spoke on "Some Problems in Graphite Crucible Manufacture."

GEFHART STEHRMAN, *Secretary*.

#### PUGET SOUND SECTION.

The Section has as its speaker, on January 20, J. F. Plaskeet, director of the Dominion Astrophysical Observatory at Victoria, B. C., who lectured on the subject, "The Chemistry of the Stars."

R. W. ELLISON, *Secretary*.



## ROCHESTER SECTION.

On February 7, F. R. Baxter, chief chemist of the Vacuum Oil Company, gave an illustrated lecture before the Section on "The Manufacture of Barrels."

ERLE M. BILLINGS, *Secretary*.

## ST. LOUIS SECTION.

The regular meeting of the Section was held on February 7, and was addressed by A. H. Compton, professor of physics at Washington University, on the subject, "Micro-World of the Atom."

H. A. CARLTON, *Secretary*.

## SAVANNAH SECTION.

At a special meeting of the Section, on January 18, the members were favored by an illustrated lecture on "The Manufacture of Dynamite and Gelatin," by E. M. Symmes, of the Hercules Powder Company. Attendance, 35.

The 5th regular meeting of the Section was held on January 27, when the following papers were presented: "The Fertilizer Industry," by E. H. Armstrong; "Potash," by P. H. Carter; and "Acid Phosphate," by P. McG. Shuey. Attendance, 42.

HERBERT P. STRACK, *Secretary*.

## SOUTHERN CALIFORNIA SECTION.

On January 27, Francis J. Pease, of the Mt. Wilson Observatory, addressed the Section on the "100-inch Reflector; its Construction and Some of the Work that is Being Done With it."

H. L. PAYNE, *Secretary*.

## TOLEDO SECTION.

At a joint meeting, between the Local Section and the Toledo Section of the American Society of Mechanical Engineers, the Toledo Case Club, the Doherty Men's Fraternity, and other engineering bodies, held on February 18, Dayton C. Miller, of the Case School of Applied Science, gave an illustrated lecture on "Sound Wave Photography."

R. W. ERWIN, *Secretary*.

## UNIVERSITY OF ILLINOIS SECTION.

The 112th regular meeting of the Section was held on January 19, at which time A. M. Buswell spoke to the members on "Some Recent Experiments in Dewatering of Sludges and Slimes."

At the 113th meeting of the Section, held on February 16, R. S. Moore, of the U. S. Bureau of Mines, spoke on the subject of "Helium."

S. A. BRALEY, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

On January 21, the members of the Section heard an address by L. H. Cone, of the National Aniline and Chemical Co. C. C. MELOCHE, *Secretary*.

## UNIVERSITY OF MISSOURI SECTION.

The 97th meeting of the Section occurred on February 4, when H. D. Hooker, Jr., read a paper on "The Function of Pentosans in Plants."

HENRY D. HOOKER, JR., *Secretary*.

## VIRGINIA SECTION.

The 40th meeting of the Section, on February 18, had as its speaker, Harrison E. Howe, who spoke on "The Division of Research Extension and its Relation to Chemistry."

ROBT. F. McCRACKAN, *Secretary*.

## WASHINGTON, D. C., SECTION.

The 315th meeting of the Section was held on February 10, at the Cosmos Club, when the following symposium on fertilizer chemistry was presented: "The Present American Fertilizer Industry," by Wm. D. Hurd; "Phosphates and Phosphoric Acid Production," W. H. Waggaman; "The Potash Situation of To-day," by F. W. Brown; "Nitrogen Resources, Possibilities and Requirements," by Capt. D. P. Gaillard; "Fertilizer Utilization, Coördination of Soil, Plant and Fertilizer," Oswald Schreiner; and "Concentrated Chemical Fertilizers, a Future Prospect," by R. O. E. Davis.

J. B. REED, *Secretary*.

## WISCONSIN SECTION.

On January 26, W. E. Tottingham addressed the Section on "The Effect of Climate on the Chemical Composition of Plants."

V. L. BOHNSON, *Secretary*.

## DECEASED.

Belden, A. W., Jones & Laughlin Steel Co., Woodlawn, Pa., died December 14, 1920.

Broeker, C. E., 5520 Blackstone Ave., Chicago, Ill.

Dewey, Frederic P., Mint Bureau, U. S. Treasury, Washington, D. C., died February, 11, 1921.

Cleary, Martin J., 1055 Loyola Ave., Chicago, Ill.

Kunz, Herman W., 1240 E. 71st St., Cleveland, O., died May, 1920.

Moore, Russell W., 44 W. 77th St., New York City, died July 31, 1920.

Yocum, John H., 325 Academy St., Newark, N. J., died Jan. 27, 1921.

# Proceedings.

## COUNCIL.

President Smith has been requested by Mrs. William Brown Meloney, who is in charge of the reception of Madame Curie in this country, to head a Reception Committee of the American Chemical Society and to appoint additional members. Doctor Smith has appointed the following, Leo H. Baekeland, Wilder D. Bancroft, B. B. Boltwood, Marston T. Bogert, Charles F. Chandler, Charles H. Herty, S. C. Lind, R. B. Moore, W. H. Nichols, W. A. Noyes, Charles L. Parsons, Ira Remsen, T. W. Richards, J. Enrique Zanetti.

In compliance with a request of the American Mining Congress that a representative of the American Chemical Society be appointed to meet with them on March 10, at 10.00 A.M., at the Biltmore Hotel, New York City, President Smith appointed Dr. Charles Baskerville.

### MEMBERS ELECTED BETWEEN FEBRUARY 15 AND MARCH 15, 1921.

Abernethy, Raymond J., 597-32nd St., Oakland, Calif.  
Aiken, Hugh K., Jr., "Hillcrest," Ithaca, N. Y.  
Allen, Charles J., 3738 Edwards Rd., Hyde Park, Cincinnati, O.  
Alsberg, Julius, 140 South Dearborn St., Chicago, Ill.  
Anthes, John F., 2132-85th St., Brooklyn, N. Y.  
Attisani, Vincent J., 39 Seventh St., New Rochelle, N. Y.  
Aultman, Paul M., 1418 Pine St., Norristown, Pa.  
Barbehenn, J. Berthold, 150 W. Broad St., Bethlehem, Pa.  
Beekley, Henry L., 1929 Kinney Ave., Cincinnati, O.  
Bellamy, B. C., 1102 Grand Ave., Laramie, Wyo.  
Bennett, John A., 168 Gold St., Dover, N. J.  
Bertram, S. H., Burgem. Meinessplein 6A, Rotterdam, Holland.  
Blanke, D. C., 49 Claremont Ave., New York, N. Y.  
Bode, J. Carl, 411 Hawthorne Ct., Madison, Wisc.  
Bodenius, J. E., 3210 Arthington Ave., Chicago, Ill.  
Bosman, V., Box 153, University Station, Urbana, Ill.  
Bowman, Jay, 6421 Harper Ave., Chicago, Ill.  
Bradford, James A., Findlay College, Findlay, O.  
Brower, P. V., 103 Andrew Pl., W. Lafayette, Ind.  
Brown, Robert E., Miami University, Oxford, O.  
Burgess, Wayland M., 21 Elbridge St., Worcester, Mass.  
Burr, G. O., Room 16, Y. M. C. A., Wichita, Kans.  
Busch, John S., 5005 Lyndale Ave. So., Minneapolis, Minn.  
Busch, K. G. A., 2424 Sherwood Rd., Bexley, Columbus, O.  
Bush, Russell J., Colfax, Ind.  
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Caldeira, Fred D., care Presbyterian Hospital, Chicago, Ill.  
Canter, Vernon C., Box 117, Bradford, Pa.  
Cargill, Everett C., 5814 Forbes St., Pittsburgh, Pa.  
Carlson, Carl E., North Main St., West Hartford, Conn.  
Carlson, Gustav, Suite No. 7, 282 Massachusetts Ave., Cambridge 39, Mass.  
Cervi, Armando, 116 Riverside Drive, New York, N. Y.  
Claypool, Walter, care The Texas Co., Bayonne, N. J.  
Cocksedge, H. E., 7 Dyar Terrace, Wintonington, Northwich, Cheshire, England.  
Cohen, Abraham, 86 Phillips St., Boston, Mass.  
Collins, O. C., 1964 Ryons St., Lincoln, Nebr.  
Cresson, Lionel, Netherlands Gutta Percha Co., Pasir Panjang, Singapore, Straits Settlements.  
Culpepper, C. W., H. P. Bur. of Plant Industry, U. S. Dept. of Agr., Washington, D. C.  
Dayton, Walter C., 581 Broad St., Newark, N. J.  
De Bar, H. L., care F. W. Freeborn Eng. Corp., Tulsa, Okla.  
Deterding, Henry C., Mueller Mfg. Co., Decatur, Ill.  
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- Flurschein, Bernard, Rushmoor, Fleet, Hampshire, England.  
 Friend, J. Newton, Technical School, Suffolk St., Birmingham, England.  
 Gadd, Edna D., 13 Main St., Plymouth, N. H.  
 Gageby, P. A., 1956 W. 94th St., Chicago, Ill.  
 Gallun, Albert F., Jr., 620 Newberry Blvd., Milwaukee, Wis.  
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 Gibson, Donald C., Martinez, Calif.  
 Giddings, W. W., 150 Langdon St., Madison, Wisc.  
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 Grinditch, Wm. H., 4003 York Road, Philadelphia, Pa.  
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 Guthrie, Horace B., 64 Putnam St., Buffalo, N. Y.  
 Hall, Archibald J., care Silver Springs Bleaching & Dyeing Co., Timberbrook, Congleton, Cheshire, England.  
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 Henley, Andrew T., Lady's Well Brewery, Cork, Ireland.  
 Hermanowich, Chas., 1855 S. California Ave., Chicago, Ill.  
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 Johns, Reinhold P., 227 Central Ave., West Hoboken, N. J.  
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 Kerry, Arthur N., Laboratorio Quimico, Alianza, Santos Lugares, P. C. Pacifico, Prov. de Buenos Aires, Argentina, S. Amer.  
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 King, W. C., 1135 N. Main St., Bethlehem, Pa.  
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 Knox, George, School of Mines, Treforest, Glamorgan, Wales.  
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 Lancaster, H., 616 Fulton St., Chicago, Ill.  
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- Miketta, Casimir, Jr., 1605 N. Kingsley Drive, Hollywood, Calif.  
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 O'Neill, Charles W., 169 Elizabeth St., Derby, Conn.  
 Oppermann, R. A., 3000 Lincoln Ave., Chicago, Ill.  
 Oyster, Leone, 204 N. Huron St., Albion, Mich.  
 Palmer, Henry F., Jr., 35 Center St., Middleboro, Mass.  
 Powers, Frederic D., 143 Ridgewood Ave., Glen Ridge, N. J.  
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 Rolls, Harold J., 481 Ellicott Sq. Bldg., Buffalo, N. Y.  
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 Rose, Edward G., 408 W. Chestnut St., Albion, Mich.  
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 Ruth, Joseph P., Jr., 4570 Wolf St., Denver, Colo.  
 Ryan, Henry T., 389 East 2nd St., Brooklyn, N. Y.  
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 Sanchez, Federico, 238 S. Thayer St., Ann Arbor, Mich.  
 Schultz, E. O., 225 Harrison Ave., Lakeview, New Orleans, La.  
 Schulzke, O. F., 8845 Portland Terrace, St. Louis, Mo.  
 Schweitzer, T. Robert, Municipal University of Akron, Akron, O.  
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 Shead, Arthur C., care Oklahoma Geological Survey, Norman, Okla.  
 Sheehan, William F., 2554 Smalley Court, Chicago, Ill.  
 Sherman, James M., Dairy Division, U. S. Dept. of Agr., Washington, D. C.  
 Smith, Arthur M., 1900 Euclid Ave., Room 808, Cleveland, O.  
 Smith, A., Gabriel Wetsustraat 24, Amsterdam, Holland.  
 Sofianopoulos, A. J., 527 Morris Ave., Elizabeth, N. J.  
 Sperry, W. M., 113 Oak Ave., Ithaca, N. Y.  
 Stack, James R., American Smelting & Refining Co., Maurer, N. J.  
 Stehle, Richard B., 5010 Penn St., Frankford, Philadelphia, Pa.  
 Steinman, F. H., Haven House, Evanston, Ill.  
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 Tsu-Pei, Pi, 1127 Bowen Court, Madison, Wisc.  
 Tuma, Vladimir, 3101 Natchez Ave., S. W., Cleveland, O.  
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 Van Horn, Jesse L., 1440 Roycraft Ave., Lakewood, Cleveland, O.  
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 Werm, Edward R., St. Cyril & Methodius Seminary, Orchard Lake, Mich.

Wertheimer, Peter, United Chemical & Organic Prod. Co., Hammond, Ind.  
 Wilcox, Harry B., Chem. Lab., Bethlehem Shipbuilding Corp., San Francisco, Calif.  
 Wilson, Alfred W., 924 Forest Ave., Ann Arbor, Mich.  
 Wilson, John A., 5 Clifton Place, Brooklyn, N. Y.  
 Wilson, Samuel, Bowne Hall, Syracuse University, Syracuse, N. Y.  
 Winter, Henry L., Jr., 824 Hartley Hall, Columbia University, New York, N. Y.  
 Woodrow, Harold W., 3113 West 101st St., Cleveland, O.  
 Wright, Harold E., care Sir B. Samuelson & Co., Ltd., Middlesbrough, England.  
 Wunderle, Fred V., 118 Pegg St., Philadelphia, Pa.  
 Yamada, Keisuke, care Japanese Consulate, 165 Broadway, New York, N. Y.  
 Ziegler, Paul F., Science Hall, Northwestern University, Evanston, Ill.

## CORPORATE MEMBERS.

Chicago Crucible Co., 2525 Clybourn Ave., Chicago, Ill.  
 Hirsch Laboratories, Inc., 50 East 41st St., New York, N. Y.  
 Roxana Petroleum Corp., Wood River, Ill.

## MEETINGS OF THE SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons,  
 1709 G St., N. W., Washington, D. C.)

## AMES SECTION.

At the regular meeting, held on February 24, the following addresses were given:  
 "The Distillation of Aqueous Solutions of Formaldehyde," by J. A. Wilkinson; and  
 "The Decomposition of Potassium Chlorate," by F. E. Brown.

H. L. MAXWELL, *Secretary*.

## CALIFORNIA SECTION.

The 121st regular meeting of the Section was held on February 18. The following program was given: "The Amino Carbonic Acids and Their Salts," by E. C. Franklin, of Stanford University; and "Production of Natural Potash Alum," by Lindsay Duncan, of San Francisco.

LYDD W. CHAPMAN, *Secretary*.

## CHICAGO SECTION.

On March 18, Lafayette B. Mendel, of Yale University, spoke before the members of the Chicago Section, on the subject: "What Constitutes a Food?"

S. L. REDMAN, *Secretary*.

## CINCINNATI SECTION.

The 241st regular meeting of the Section occurred on March 9, when H. W. Jordan, of the Somet-Solvay Company, spoke on "The Solvay Chemical Industries; Their Work in War and Peace."

CARL H. LUND, *Secretary*.

## COLORADO SECTION.

At the regular meeting of the Section, on February 28, R. G. Gustavson gave a paper on "Some Application of the Electron Theory to Chemistry."

RUTH B. VUTRUBBS, *Secretary*.

## CONNECTICUT VALLEY SECTION.

On March 18, Harry N. Holmes, of Oberlin College, spoke before the Section on "Gels and the Application of Colloidal Chemistry."

HARRY WISSELS, *Secretary*.

## CORNELL SECTION.

The regular meeting of the Section was held on February 28, when O. A. Johannsen addressed the members on "Poisonous Insects and the Poisons of Insects."

F. R. GEORGIA, *Secretary*.

## DELAWARE SECTION.

Marston T. Bogert, of Columbia University, addressed the members of the Section, March 23, on "Science and Disarmament."

FRED C. ZEISSBERG, *Secretary*.

## DETROIT SECTION.

The 123rd meeting of the Local Section was held on February 16. The address of the evening was by Carl Thieme, of the Michigan Smelting and Refining Co., who spoke on "The Physical Metallurgy of the Non-ferrous Metals."

The 124th meeting of the Section occurred on March 16, when F. O. Taylor, of Parke, Davis & Company, spoke on "The Vitamines."

WM. B. TEMPLETON, *Secretary*.

## GEORGIA SECTION.

The members of the Georgia Section were the guests of the Atlanta Chapter of the American Institute of Electrical Engineers, on February 25. The speaker, Charles G. Adsit, addressed the meeting on the subject of "Rainfall."

J. S. BROGDON, *Secretary*.

## INDIANA SECTION.

William J. Hale, of the Dow Chemical Company, Detroit, Mich., addressed the meeting of the Section on February 18, his subject being "The Immediate Needs of Chemistry in America." W. M. Blanchard, of DePauw University, spoke on "Chemistry in the Service of Medicine." Attendance, 31%.

On March 11, the members of the Section were addressed by Mungo E. Nasmith, superintendent of the Commercial Solvents Company, at Terre Haute, Ind., on the subject, "Butyl Alcohol and Acetone from Corn." Attendance, 32%.

EDGAR B. CARTER, *Secretary*.

## KANSAS CITY SECTION.

The regular February meeting of the Section was held in Lawrence, Kansas, on February 19, in a joint program with the 53rd annual meeting of the Kansas Academy of Science. There were presented during the sessions of the two organizations 46 papers on various scientific subjects.

LEE E. CLARK, *Secretary*.

## LEXINGTON SECTION.

The 68th meeting of the Section was held on February 25. A paper was read by C. A. Shull on "The Magnitude of Some Natural Forces." Attendance, 26%.

S. D. AVERITT, *Secretary*.

## LOUISIANA SECTION.

On February 18, Robert Glenk, Curator of the State Museum, presented a paper before the Section on "Louisiana Lignite," illustrated with lantern slides and specimens. At this meeting the following officers were elected for 1921: H. W. Moseley, *President*; C. L. Clay, *Vice-President*; H. R. Stevens, *Secretary*; F. W. Liepsner, member *Ex-Officio*; and Charles E. Coates, *Councilor*.

H. R. STEVENS, *Secretary*.

## LOUISVILLE SECTION.

At the regular monthly meeting of the Section, held on February 18, R. L. Beakes, of the Louisville Lead and Color Company, gave a talk on the subject of "Paints and Varnishes."

C. E. GEIGER, JR., *Secretary*.

## MICHIGAN AGRICULTURAL COLLEGE SECTION.

On January 19, at a luncheon given by the Section, a roll call was responded to by the names of eminent scientists and a brief statement of their best-known works given. Attendance, 50%.

D. T. Ewing spoke before the members on January 25 in the Kedzie Chemical Laboratory, his subject being "The Electrometric Titration of Oxidation and Reduction Reactions." Attendance, 75%.

At the regular meeting of the Section, held on February 9, C. E. Bement, of the Novo Engine Company, Lansing, Mich., spoke on the present industrial situation. Attendance, 50%.

C. S. ROBINSON, *Secretary*.

## MILWAUKEE SECTION.

On March 18, C. B. Dickey, of the Corona Chemical Company, addressed the Section on the subject of "Some Chemical Facts and Theories of Operative Photography."

O. A. CHERRY, *Secretary*.

## NASHVILLE SECTION.

The Section had as its speaker on March 7 George E. Marton, of The Barrett Company, whose subject was "The Chemistry and Methods of Wood Preservation," illustrated with lantern slides and moving picture films.

H. A. WEBB, *Secretary*.

## NEBRASKA SECTION.

At a special meeting of the Section, held on February 19, S. B. Arenson reported on "A New Quantitative Method for the Determination of Potassium in Potash Waters."

J. C. Russell, of the University of Nebraska, spoke before the Section, March 24, on "Acidity of Nebraska Soils."

SAUL B. ARENSEN, *Secretary*.

## NEW HAVEN SECTION.

At a meeting of the Section on March 1, R. Dawson Hall, editor of *Coal Age*, spoke on "The Coal Industry."

BLAIR SAXTON, *Secretary*.

## NEW YORK SECTION

On March 11, Frank G. Breyer, chief of the research division of the New Jersey Zinc Company, spoke before the meeting of the Section on "Paint and Rubber Pigments."

H. G. SIDEBOTTOM, *Secretary*.

## NORTHEASTERN SECTION.

The 165th regular meeting of the Section, held on March 11, had the following addresses: "Aluminum and Its Light Alloys," by Robert S. Williams; and "Modern Smokeless Powder," by Tenney L. Davis.

L. F. HAMILTON, *Secretary*.

## OKLAHOMA SECTION.

The mid-winter meeting of the Oklahoma Section was held on February 12 at the University of Oklahoma, Norman, Okla. The following program was carried out: "A Neglected Test for Morphine," by Guy Y. Williams; "Changes in the Composition of the Fat of Peanut-Fed Rabbits during Starvation," by C. T. Dowell; "Colloid Chemistry and Petroleum," by Fred A. Padgett; "Relations between Granular Electricity, Atomic Structure and Valence," by A. F. Reiter; "Metallic Soaps," by Hilton Ira Jones; "The Separation of Caffeine from Cocaine-Allied Alkaloids from Syrups Used in Soft Drinks," by Edwin DeBarr; and "The Manufacture of Alcohols and Other By-Products from Petroleum," by Sidney Born.

HILTON IRA JONES, *Secretary*.

## OREGON SECTION.

On February 26, at the regular monthly meeting of the Section, held at the Seward Hotel, Portland, Oregon, the following addresses were given: "The Western Beet Sugar Industry," by E. W. Lazell; and "Some of the Less Common Sugars," by H. R. Kelly.

The following officers have been elected to serve for 1921: Ralph K. Strong, chairman; H. G. Miller, vice-chairman; Page R. Boyles, Secretary-treasurer; and John F. Fulton, councilor.

At the regular meeting of the Section, held at Reed College, the following addresses were given: "Industrial Uses of City Gas," by E. L. Hall, General Superintendent of the Portland Gas and Coke Company; and "Combustible Gases, Their Characteristics and Recent Developments," by R. K. Strong, of Reed College.

PAGE R. BOYLES, *Secretary*.

## PHILADELPHIA SECTION.

The regular monthly meeting of the Section occurred on March 17, at the Engineers' Club, Philadelphia, when James F. Norris, of Massachusetts Institute of Technol-



ogy, spoke on "Recent Progress in Organic Chemistry." At the usual informal dinner, the address was given by William Martin, of Philadelphia, who spoke on "A Glimpse of the Traffic Man's Point of View."

J. HOWARD GRAHAM, *Secretary*.

#### PITTSBURGH SECTION.

The annual smoker of the Section was given on February 24 at the U. S. Bureau of Mines Building, Pittsburgh, Pa.

On March 17, E. M. Chamot, of Cornell University, addressed the Section on the subject of "Industrial Microscopy."

GERHARD STEGEMAN, *Secretary*.

#### PUGET SOUND SECTION.

The regular monthly meeting of the Section occurred on February 23, when George E. Whitwell, of the University of Washington, spoke on the subject: "Efficiency and Economy in the Manufacture, Distribution, and Utilization of Illuminating Gas."

R. W. ELLISON, *Secretary*.

#### ROCHESTER SECTION.

Dr. Edgar F. Smith, President of the American Chemical Society, addressed the members of the Rochester Section on the evening of February 21. An informal dinner in honor of Doctor Smith was served at the Rochester Club.

The 120th meeting of the Section occurred on March 7, at the University of Rochester, when Edward B. Leary, of the Leary Dye Works, discussed the subject of "Where and How the Chemist Helps in an Ordinary Business." His talk was illustrated by experiments and lantern slides.

ERLE M. BILLINGS, *Secretary*.

#### ST. LOUIS SECTION.

H. A. Carlton, of the Mallinckrodt Chemical Works, read a paper before the regular monthly meeting of the Section, March 7, on "Arsphenamine."

H. A. CARLTON, *Secretary*.

#### SAVANNAH SECTION.

The following papers were read before the members of the Local Section on March 3: "The Economic Position of Cottonseed Oil," by B. F. Taylor; and "By-Product Coke Ovens and the Manufacture of Ammonium Sulfate," by A. B. Carmichael. Attendance, 36.6%.

HERBERT P. STRACE, *Secretary*.

#### SOUTHERN CALIFORNIA SECTION.

Two connected lectures, on February 18 and 19, on the subject of "Structure of the Atom," were delivered by Robert A. Millikan, professor of physics, University of Chicago, before a joint meeting of the local sections of the American Chemical Society, American Institute of Electrical Engineers and the Mathematics and Science Association.

H. L. PAYNE, *Secretary*.

#### SOUTHEAST TEXAS SECTION

On March 19, the following program was given before the Section: "The Manufacture of Casing Head Gasoline," by Frank Seibert, of the Gulf Pipe Line Company; and "The Transportation of Oil," by Charles Fitzgerald, Jr., of the White Oil Company.

P. S. TILSON, *Secretary*.

#### SOUTH JERSEY SECTION.

The 6th regular meeting of the Section was held on February 16 at the du Pont Club. H. D. Gibbs spoke on "Palm Trees as a Commercial Source for Alcohol and Sugar." Attendance, 63%.

C. E. BURKE, *Secretary*.

#### SYRACUSE SECTION.

A meeting of the Section was held on February 11, when A. G. Carmen, of Syracuse, gave a lecture on "Principles and Practice of Die Castings." Attendance, 8½%.

The 147th meeting of the Section occurred on February 25, when James Kendall, of Columbia University, spoke on "A Modified Ionization Theory."

An extra winter meeting of the Section was held on March 4 in the Chamber of Commerce, in the form of a joint banquet with the Society of Steel Treathers; John A. Mathews, president of the Crucible Steel Company, speaking on the advances made by that company in the manufacture of high-grade steels for special purposes.

BYRON W. GRIMES, *Secretary*.

#### TOLEDO SECTION.

L. V. Redman, president of the Redmanol Chemical Products Company, of Chicago, spoke on "Synthetic Phenol Resins," at the regular monthly meeting of the Section, held on March 11.

R. W. ERWIN, *Secretary*.

#### UNIVERSITY OF ILLINOIS SECTION

At the regular meeting of the Section, held on March 15, Farrington Daniels, of the University of Wisconsin, spoke to the members on the subject of "The Radiation Hypothesis and Reaction Velocity."

S. A. BRALBY, *Secretary*.

#### UNIVERSITY OF MICHIGAN SECTION.

On March 1, A. E. White, of the University of Michigan, spoke before the Section on the subject: "The Constitution and Properties of Boiler Tubes."

C. C. MELOCHE, *Secretary*.

#### VIRGINIA SECTION.

The 41st meeting of the Section was held on March 18, when Hugh S. Taylor addressed the members on "Pure Research in the Development of Industrial Catalysis."

ROBERT F. MCCrackAN, *Secretary*.

#### WASHINGTON, D. C., SECTION.

The 315th meeting of the Section was held at the Cosmos Club on March 10, when the following addresses were given: "Chemical Crystallography," by E. T. Wherry; and "X-Ray and Crystal Structure," by R. W. G. Wyckoff.

J. B. REED, *Secretary*.

#### WISCONSIN SECTION.

At the regular monthly meeting of the Section, held on February 23, V. L. Bohnsen spoke on "Some Recent Researches on the Catalytic Decomposition of Hydrogen Peroxide."

On March 16, David Fahlberg, of the Department of Chemical Engineering, spoke before the members of the Section on "Some Micro-Chemical Studies of Steel."

V. L. BOHNSON, *Secretary*.

#### DECEASED.

Hinds, J. I. D., 1718 West End Ave., Nashville, Tenn., died March 4, 1921.

Kuzirian, Simon B., Box 87, Jamaica, L. I., died Feb. 5, 1921.

Olin, F. W., Jr., 1128 Saate St., Alton, Ill., died Feb. 4, 1921.

Ruffle, John, Musley Hill, Ware, Herts, England, died Nov. 19, 1920.

# Proceedings.

## Minutes of the Directors Meeting.

The Directors of the American Chemical Society met at Mechanics Institute, Rochester, April 27, 1921, at 3.00 p. m., with President Smith in the chair and the following Directors present: Bancroft, Bigelow, Little Rosengarten, Talbot, and Parsons.

The Council having unanimously voted

That this Council expresses to the Directors of the Society the hope that the Eschenbach Printing Company will be released from any forfeits that may arise under the terms of its contract in connection with the impending strike, due to the insistence upon the 44-hour week, and

That the members of this Council speaking for the members of their local sections also express their full willingness, in the event such a strike is not amicably settled, to wait indefinitely for the publication of the journals of the Society

and the Advisory Committee and several of the local sections of the American Chemical Society having also expressed their agreement with the above vote, the Directors unanimously voted to release the Eschenbach Printing Company from all forms of penalties or forfeits that might arise under the current terms of its contracts with the American Chemical Society in the event of a delay in the publication of the Society's journals incident to such strike, and they further voted that the Directors would agree to any temporary suspension of publication necessary.

It was voted to authorize the editors of the Society's journals to destroy any letter files and manuscript files over two years old no longer required, in their opinion, for the proper conduct of their offices.

The Directors voted to authorize the Treasurer to pay a bill of \$17.50 from Incidental Account incurred by the chairman of the Committee on Occupational Diseases.

The Treasurer announced the purchase of temporary securities as follows:

February 9, 1921, Two 90-day Bank of America Acceptances, due May 10, 1921, yielding  $6\frac{1}{8}\%$ . Cost \$13,962.93.

March 6, 1921, One City of Memphis 6% Tax Anticipation Note at 99.8802, due Sept. 1, 1921. Cost \$9,988.02.

March 24, 1921, Two City of Spartanburg 6% Tax Anticipation Notes, due August 19, 1921. Cost \$10,021.89.

This action received the approval of the Directors.

The Directors voted to authorize the Treasurer in case of necessary absence from his office to delegate the signing of routine and other necessary Society checks to a member of the Finance Committee as his attorney, "and that the Farmers' Loan & Trust Company be authorized to pay all checks when signed by a member of the Finance Committee, having previously been advised by the Treasurer of the appointment of such member as his attorney."

The Directors voted to authorize the Treasurer to open a separate account, entitled "American Chemical Society Account No. 2" in the Farmers' Loan & Trust Company, and to deposit therein checks drawn on his regular account covering a number of small items in one collective bill, such as Abstractors and Assistant Editors' checks, etc., and to cover the checks on his regular account by one voucher, as suggested by the auditors and outlined in his letter of April 25, 1921, to the Secretary of the

Society. They further voted to authorize him to delegate authority to sign checks on this special account, covering the numerous items included in the one voucher, to A. J. Marratt, his secretary, "and that the Farmers' Loan & Trust Company be authorized to pay any checks signed by A. J. Marratt, Attorney, on the account of the Society entitled American Chemical Society Account No. 2."

The Directors then adjourned.

CHARLES L. PARSONS, *Secretary*.

## COUNCIL.

President Edgar F. Smith has appointed Dr. George B. Frankforter to represent the American Chemical Society at the inauguration of Dr. Lotus Delta Coffman as President of the University of Minnesota, to be held on May 13, 1921.

Dr. Thomas G. Delbridge, of the Atlantic Refining Co., Philadelphia, Pa., at the request of President Smith, represented the Society as its delegate at a meeting held under the auspices of the American Petroleum Institute in New York City, April 11, to consider uniform testing methods, the ways and means of procuring their adoption by the oil industry, and the establishment of a method of arbitration in disputes over oil tests.

### MEMBERS ELECTED BETWEEN MARCH 15 AND APRIL 15, 1921.

Adams, James Edward, 222 Marsteller St., West Lafayette, Ind.  
 Aldridge, Alfred Edward, 22 Ngata St., Palmerston North, New Zealand.  
 Allen, Raymond P., Lima, N. Y.  
 Allison, A. E., B. Medberry Hobart College, Geneva, N. Y.  
 Anderson, Daved E., Augustana College, Rock Island, Ill.  
 Armstrong, Paul L., 284 Franklin Ave., River Forest, Ill.  
 Aydelotte, J. T., 207 Alberta Corner, Calgary, Alta., Canada.  
 Babcock, E. B., 428 N. Firestone Blvd., Akron, O.  
 Barthels, Herbert W., 41 Second St., National City, Calif.  
 Bassett, James W., 743 McMackin Ave., Winton Place, Cincinnati, O.  
 Berman, Harry, 116 Nonotuck St., Holyoke, Mass.  
 Birkner, Victor, 552 14th St., S. E., Washington, D. C.  
 Boley, Conrad H., 50 N. Aberdeen Place, Atlantic City, N. J.  
 Bowen, C. W., Brunswick, Mo.  
 Bradbeer, Chester B., 126 N. Hartwick, Eagle Rock City, Calif.  
 Brewer, Robert K., 706 Maryland Ave., Syracuse, N. Y.  
 Bruce, James, The Technical College, Huddersfield, England.  
 Burns, Kevin, Allegheny Observatory, Pittsburgh, Pa.  
 Caulkins, Asa L., 530 E. Walnut St., Stockton, Calif.  
 Cavanaugh, Geo. W., 217 Willard Way, Ithaca, N. Y.  
 Chen, Yu Gwan, 1116 Amsterdam Ave., New York City.  
 Cloke, John B., Hoosick, N. Y.  
 Council, Frank E., Texas Christian University, Forth Worth, Tex.  
 Craig, Paul S., Bowne Hall, Syracuse University, Syracuse, N. Y.  
 Curtis, Arthur James, 3277 W. 98th St., Cleveland, O.  
 Dalton, John N., 900 Hope St., Providence, R. I.  
 Dicks, Charles B., Jr., 34 Dana St., Cambridge, Mass.  
 Dunkle, Cyrus G., 1125 Hillsdale Ave., Dormont, Pa.  
 Durham, Hobart N., Suite 9, 84 St. Botolph St., Boston, 17, Mass.  
 Edlund, Karl R., 1233 3rd Ave., Oakland, Calif.  
 Everhart, W. Alfred, P. O. Box 564, Granville, O.  
 Fischer, Arthur H., 223 Ohio Ave., Providence, R. I.  
 Flett, Raymond L., 325 W. 3rd St., Cincinnati, O.  
 Fowlkes, Floyd E., John Marshall High School, Richmond, Va.  
 Friedman, Joseph S., National Aniline & Chemical Co., Buffalo, N. Y.  
 Gilfillan, F. A., 954 Yale Station, New Haven, Conn.  
 Hall, Sydney H., 59 Cheriton Road, Wollaston, Mass.  
 Harrison, George F., 260 Olney St., Providence, R. I.  
 Havighurst, R. J., 130 N. Washington St., Delaware, O.

- Head, John P., 3 Cambridge St., Concord, N. H.
- Hilton-Brown, Edward, Maguire, Paterson & Palmer, Ltd., Pembroke, Ont., Canada.
- Horton, Paul M., Louisiana State University, Baton Rouge, La.
- Horwitz, Nathan C., 433-35 Hopkinson Ave., Brooklyn, N. Y.
- Humboldt, E., Mason By-Products Co., Sausalito, Calif.
- Hurd, William D., 236 Southern Bldg., Washington, D. C.
- Hurst, Charles R., Div. Plant Pathology & Botany, University Farm, St. Paul, Minn.
- Ishibashi, Masayoshi, 3038 Yasashi-mura, Kaijo-gun, Chiba-Ken, Japan.
- Ishikawa, Takuji, c/o Kenkyubu, Mitsui Dyestuff & Chemical Works, Omuta, Fukuokaken, Japan.
- Jacobs, Albert L., 98 Fuller St., Brookline, Mass.
- Jenkins, S. S., Box 334, West Durham, N. C.
- Johnson, Herbert F., Jr., 810 University Ave., Ithaca, N. Y.
- Jones, Augustus, 168 Hoosick St., Troy, N. Y.
- Jones, Wm. Catesby, 6 North 2nd St., Richmond, Va.
- Keane, Charles A., The Sir John Cass Technical Institute, Jewry Street, Aldgate, London, E. C. 3, England.
- Keeny, J. Roy, Louisiana State Board of Health, New Orleans, La.
- Kessler, J. Rissel, 5028 Schuyler St., Philadelphia, Pa.
- Kimberly, H. S., 1440 R St., N. W., Washington, D. C.
- King, W. C., 1220 Clinton St., Buffalo, N. Y.
- Klain, Joshua J., 5930 Spring St., Philadelphia, Pa.
- Kunitz, M., 436 East 67th St., New York City.
- Lamb, Harold, 49 Dodworth Road, Barnsley, Yorkshire, England.
- Larmour, R. K., University of Saskatchewan, Saskatoon, Sask., Canada.
- Lawler, William P., S. C. Johnson & Son, Racine, Wis.
- Lloyd, W. M., 67 Hammond St., Cambridge, Mass.
- Logue, Paul, Atlantic Dyestuff Co., Burrage, Mass.
- Losanitch, M., Institute de Chimie, University of Belgrade, Belgrade, Serbia.
- Lucas, Cyril C., 1113 Erato St., New Orleans, La.
- Manning, J. Ruel, 1109 AOUW Building, Little Rock, Ark.
- Marsman, J. H., Malabon Sugar Co., Manila, P. I.
- Martin, J. W., Chief Chemist, E. and M. Services, Baghdad, Mesopotamia.
- Matsuda, Ryoichi, Sakuradori 2, Okamachi, near Osaka, Japan.
- Matsuura, Ryosaku, The Central Lab., S. M. R. Co., Dairen, Manchuria.
- McLellan, Basil G., Rowntree & Co., Ltd., The Cocoa Works, York, England.
- Miles, J. Lawrence, 35 Merrima St., Lexington, Mass.
- Mills, Bruce H., Pikeville, Tenn.
- Naar, Alexander, 112 Hancock East, Detroit, Mich.
- Naberschmig, Edw. M., Jr., 3206 St. Peter St., New Orleans, La.
- Naito, Koichi, 1318 7th St., S. E., Minneapolis, Minn.
- Nixon, H. T., C & C Developing Co., 13th & Winchester, Kansas City, Mo.
- Ohso, J. G., 2074 Mohegan Ave., Apt. 2A, The Bronx, New York City.
- Ono, Yusuke, Muromachi Ebisugawa Agar, Kamigyo, Kyoto, Japan.
- Oshima, Shigeyoshi, 17 Ichichome, Nihonyenokicho, Shibaku, Tokyo, Japan.
- Perlstein, Leonard, 1380 Prospect Ave., Bronx, New York City.
- Pond, Alfred W., East Campus, State College, Pa.
- Potvliet, Michiel P. C., 395 Kingstreet West, Chatham, Ont., Canada.
- Priest, Benjamin H., 817 Rebecca Place, Elizabeth, N. J.
- Rainey, W. L., 228 B West, Hutchinson, Kans.
- Reck, Carlyle, 1000 Russell Ave., N., Minneapolis, Minn.
- Rethers, Theodore C., 499 21st Ave., San Francisco, Calif.
- Robertson, Judson H., Box 1051, University of Tennessee, Knoxville, Tenn.
- Rosenstein, A., 909 Cleveland St., Durham, N. C.
- Russell, H. E., 114 E. Walnut St., Ashland, O.
- Sachs, Ward H., 143 Hill St., Fayetteville, Ark.
- Samson, Meyer, 195 Exchange St., Rochester, N. Y.
- Sanborn, Paul H., 1435 4th Ave., Huntington, W. Va.
- Sanford, Baalis, c/o U. S. R. S., Saco, Mont.
- Sattes, Frederick L., Box 42, Lexington, Va.
- Schuback, John D., 485 Garson Ave., Rochester, N. Y.
- Shiba, Koreschige, 43 Shiocho 3-chome, Yotsuya-ku, Tokyo, Japan.
- Shipherd, John J., Delta Tau Delta House, Bethlehem, Pa.
- Slate, M. E., 7 Hudson Terrace, Dobbs Ferry, N. Y.
- Smith, C. R., P. O. Box 133, A. & M. College, College Station, Tex.
- Snyder, J. O., Western Meat Co., South San Francisco, Calif.

Spencer, H. G., Amalgamated Sugar Co., Lewiston, Utah.  
 Stark, Daniel C., West Line, Mo.  
 Stauffer, Edwin S., 838 W. Washington St., Petersburg, Va.  
 St. Clair, Palmer, Jr., P. O. Box 940, Roanoke, Va.  
 Stirnimann, Edourd, Avenue du Mail 12, Neuchatel, Switzerland.  
 Sykora, James, 175 Harrison St., Batavia, Ill.  
 Syvertsen, Chr. H. A., Brevik, Norway.  
 Takashige, Senichii, Chem. Inst., College of Science, Imperial Univ., Kyoto, Japan.  
 Takenchi, Ryozo, Chem. Lab., College of Science, Imperial Univ., Kyoto, Japan.  
 Tanabe, Tomojiro, Sumitomo Shindosho, Ajikawa, Osaka, Japan.  
 Taylor, Henry B., 1003 Pennsylvania Ave., Warren, Pa.  
 Teagle, Walter C., 26 Broadway, New York City.  
 Thomson, Hugh L., 26 Griswold St., Meriden, Conn.  
 Thomson, Joe Lee, Georgetown, Tex.  
 Thuor, Louis, 2558 Creston Ave., The Bronx, New York City.  
 Topley, Bryan, 104 Park Lane, Croydon, Surrey, England.  
 Valentine, Warren P., 320 Highland Ave., Haddonfield, N. J.  
 Vallez, H. A., 205 Mountain St., Bay City, Mich.  
 Visger, Roy F., 508 N. Lansing St., Mt. Pleasant, Mich.  
 Vollrath, Richard, 1382 1st Ave., New York City.  
 Werking, Leroy C., Hotchkiss School, Lakeville, Conn.  
 Westover, F. Murray, 38 Turner St., Plymouth, Pa.  
 Whidden, Foster C., 12 Hachfeld Rd., Worcester, Mass.  
 Whitney, Gary M., Midwest Refining Co., Casper, Wyo.  
 Willcox, Margaret F., 208 South East Ave., Oak Park, Ill.  
 Wilson, Andrew, Springfield, N. J.  
 Woehrie, Paul P., 105 Belmont Apts., 34th & Spring Garden Sts., Philadelphia, Pa.  
 Young, William, 14 Sorbie Road, South Beach, Saltcoats, Ayrshire, Scotland.

#### CORPORATION MEMBERS.

Quaker City Rubber Company, Wissinoming, Philadelphia, Pa.

## MEETINGS OF THE SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

#### CALIFORNIA SECTION.

The 122nd regular meeting of the Section was held on March 18 at the San Francisco Commercial Club, when the following program was given: "The Present Status of Chemical Criteria in the Field of Soil Fertility," by John S. Burd, of the University of California; and "Experimentation at the Temperature of Liquid Hydrogen," by Wendell M. Latimer, of the University of California. LLOYD W. CHAPMAN, *Secretary*.

#### CINCINNATI SECTION.

The 242nd regular meeting of the Section occurred on April 11, at the University of Cincinnati. J. Howard Mathews, chairman of the Chemistry Department, University of Wisconsin, gave an illustrated lecture on "Color Photography."

CARL H. LUND, *Secretary*.

#### COLUMBUS SECTION.

On April 16, the Section had as its speaker, J. Howard Mathews, of the University of Wisconsin, who spoke on "Photo-Chemistry."

MARION HOLLINGSWORTH, *Secretary*.

## CORNELL SECTION.

V. A. Moore, dean of the New York State Veterinary College, spoke before the Section, March 29, on "Chemical Problems in Immunity." F. R. GEORGIA, *Secretary*.

## DETROIT SECTION.

The 124th meeting of the Section was held on April 15, when J. Howard Mathews spoke before the members on "Photo-Chemistry." WM. B. TEMPLETON, *Secretary*.

## EASTERN NEW YORK SECTION.

C. B. Welter, of the General Electric Co., addressed the members of the Section, March 17, on the subject of "X-Rays in Medical Diagnosis."

On April 8, Matthew A. Hunter, of the Rensselaer Polytechnic Institute, spoke before the Section on "Some Electrical Properties of Alloys."

MARY R. ANDREWS, *Secretary*.

## INDIANA SECTION.

The Indiana Section held its regular monthly meeting on April 8, when E. W. McCullough spoke on "Flotation." Attendance, 23%. EDGAR B. CARTER, *Secretary*.

## LEHIGH VALLEY SECTION.

On April 1, Edgar F. Smith, President of the American Chemical Society, addressed the members of the Section on "Early Organic Chemistry in America." Attendance, 55%.

At the business meeting held on this date the following officers were elected: John T. Little, *Vice-Chairman*; E. C. Bingham, *Senior Councilor*, and R. N. Boyd, *Junior Councilor*. Resolutions adopted by the University of Illinois Section, dated November, 16, 1920, were ordered placed on file and no action to be taken at this time. Resolutions favoring the adoption of the metric system were favorably reported and will be presented at the Rochester meeting. A membership committee was appointed to take charge of a campaign to solicit new members for the Society. J. G. SKULL, *Secretary*.

## LEXINGTON SECTION.

The 69th meeting of the Section was held at the University of Kentucky, on March 23, when O. J. Stewart spoke on "The Technique of Atomic Weight Determinations by the Silver Method." Attendance, 44%.

S. D. AVERITT, *Secretary*.

## LOUISIANA SECTION.

The 135th regular meeting of the Section occurred on March 18, when two papers were presented by S. A. Mahood, of Tulane University, as follows: "The production of American Storax from the Red Gum Tree" (illustrated); and "Comparison of Wood Cellulose and Cotton Cellulose."

The 136th meeting of the Section was held on April 15. Harry B. Weiser, of Rice Institute, Houston, Tex., addressed the members on the subject of "Colloidal Chemistry."

H. R. STEVENS, *Secretary*.

## MICHIGAN AGRICULTURAL COLLEGE SECTION.

On April 14, J. Howard Mathews, of the University of Wisconsin, spoke before the members on the subject, "Photo-Chemistry."

C. S. ROBINSON, *Secretary*.

## MIDLAND SECTION.

At the regular monthly meeting of the Section, held on April 13, J. Howard Mathews addressed the members on "Photo-Chemistry."

C. C. KENNEDY, *Secretary*.

## NASHVILLE SECTION.

On March 18, a phosphate symposium was held by the Section, when the following speakers addressed the members of the Section: Lucius P. Brown, former State Food and Drug Commissioner of Tennessee; James A. Barr, chief engineer, International Agricultural Corporation, Mount Pleasant, Tenn., and Wm. R. Austin, chief chemist, Tennessee Chemical Co., Nashville, Tenn.

H. A. WEBB, *Secretary*.

## NEW HAVEN SECTION.

The regular monthly meeting of the Section occurred on March 31, in Kent Chemical Laboratory. Hugh S. Taylor, of Princeton, spoke on "Scientific Research and the Development of Industrial Catalytic Processes."

On April 25, C. H. Mathewson addressed the members on the subject, "Rolled Zinc."

BLAIR SAXTON, *Secretary*.

## NORTHEASTERN SECTION.

The 166th regular meeting of the Section occurred on April 8, at the Engineers' Club, Boston, Mass. The following program was given: "Publicity," by J. W. Harrington, technical manager of the American Chemical Society News Service; "Some Chemical Problems Connected with the Vat Dyes," by James B. Conant, of Harvard University; and "The Enamelling of Sheet Steel," by Earle P. Stevenson, of Arthur D. Little, Inc.

L. F. HAMILTON, *Secretary*.

## PHILADELPHIA SECTION.

On April 21, the following program was given by the Section: "Recent Developments of the Work of the Bureau of Standards," by W. C. Wagner, assistant to chief engineer, Philadelphia Electric Company; "Refractometry," by Warren P. Valentine. The after-dinner address was given by Richard Spillane, financial editor of the Public Ledger, who spoke on "How to Reach our Friends, the Public."

J. HOWARD GRAHAM, *Secretary*.

## PITTSBURGH SECTION.

R. F. Bacon, of the Mellon Institute, spoke before the Section on April 21, his subject being "Technology of the American Sulphur Industry."

GEBHARD STEGEMAN, *Secretary*.

## PUGET SOUND SECTION.

At the regular monthly meeting of the Section, held on March 23, Mrs. Zahlia Jencks Gailey, spoke on "Some Chemical Aspects of Electro-Plating."

R. W. ELLISON, *Secretary*.

## RHODE ISLAND SECTION.

On March 18, an illustrated lecture was given before the Section by J. C. Olsen, of the Brooklyn Polytechnic Institute, his subject being "The Manufacture of Starch Glucose and Dextrine from Corn."

HERBERT F. DAVISON, *Secretary*.



## ROCHESTER SECTION.

The 121st regular meeting of the Section was held on March 21. C. E. Kenneth Mees gave an illustrated lecture on "Measuring Stars by Light Waves."

The 122nd regular meeting occurred on April 4, when Donald W. Howe, chief chemist, Beechnut Packing Co., spoke on "Foods and Science."

On April 18, Carl L. Alsberg, formerly chief chemist of the Bureau of Chemistry, Department of Agriculture, Washington, D. C., addressed the members on the subject, "Has the Federal Government a Policy in Science and Research?"

ERLE M. BILLINGS, *Secretary*.

## ST. LOUIS SECTION.

At the regular monthly meeting of the Section, held on April 4, the following program was given: "The Distillation of Missouri Oaks, by K. K. Kershner; and "The Preparation and Properties of Furfural and Some of the Derivatives of Furfural," by M. S. Badollet and H. L. Dunlap.

H. A. CARLTON, *Secretary*.

## SOUTHERN CALIFORNIA SECTION.

The regular monthly meeting of the Section occurred on March 31, when Frederick Bulpitt, director in charge of the Metabolic Research Clinic Laboratory of the White Memorial Hospital, spoke on the subject, "The Chemical Examination of the Blood."

H. L. PAYNE, *Secretary*.

## SOUTH JERSEY SECTION.

The 7th regular meeting of the Section was held on March 24. Roger Williams spoke on "Conducting Research."

C. E. BURKE, *Secretary*.

## SYRACUSE SECTION.

The 149th meeting of the Section occurred on March 25, when William H. Walker, of Boston, Mass., spoke on "Research Methods."

B. W. GRIMES, *Secretary*.

## TOLEDO SECTION.

On March 23, P. E. Landolt, of New York City, manager of the Commercial Department of the Research Corporation, gave a lecture on "Cottrell Electrical Precipitation," illustrated with slides and motion pictures. Attendance, 84.

J. Howard Mathews, of the University of Wisconsin, addressed the members of the Toledo Section, April 12, on "Color Photography."

## UNIVERSITY OF MICHIGAN SECTION.

At the regular meeting of the Section, held on March 29, D. M. Lichty spoke before the members on the subject, "The Action of the Insoluble Oxides, Hydroxides and Carbonates on Ammonium Chloride."

C. C. MELOCHE, *Secretary*.

## VIRGINIA SECTION.

The 42nd meeting of the Section occurred on April 15. Graham Edgar addressed the members on "Chemical Combination and the Nature of Valence."

ROBERT F. MCCracken, *Secretary*.

## WASHINGTON, D. C., SECTION.

The 317th meeting of the Section was held on March 25, the following lectures being given: "Chemical Industry from the Tariff Standpoint," by C. R. DeLong; and "The Tariff on Certain Minerals used in Chemical Industries," by F. L. Hess.

The 318th meeting of the Section, held on April 14, had as its speaker, Dr. Edgar F. Smith, President of the American Chemical Society, who spoke on "A Glance at the Early Organic Chemistry of the United States."

J. B. READ, *Secretary*.

## WISCONSIN SECTION.

On March 23, E. D. Fahlberg, of the Department of Chemical Engineering, University of Wisconsin, spoke before the Section on "The Chemical Macroscopy of Metals."

V. L. BOHNSON, *Secretary*.

## DECEASED.

Hasslacher, Jacob, 709 Sixth Ave., New York, N. Y.

Pennock, J. D., Solvay Process Co., Syracuse, N. Y.

# Proceedings.

## GENERAL MEETING MINUTES.

The 61st general meeting of the American Chemical Society was held at Rochester N. Y., Monday, April 25, to Friday, April 29, 1921, inclusive. The Council meeting was held on the 25th, the general meeting on the morning and afternoon of the 26th, divisional meetings all day Wednesday and Thursday, and excursions on Friday. Full details of the meeting and program will be found in the May issue of the *Journal of Industrial and Engineering Chemistry*. The registration was 1139, and 1270 sat down to dinner at the Good Fellowship Meeting.

General public addresses were given by Senator James W. Wadsworth, Jr., on "Some Problems of National Defense," and by Congressman Nicholas Longworth, on "The American Chemical Industry and Its Need for Encouragement and Protection." At the general business meeting held Tuesday morning, April 26th, Charles F. Chandler and William H. Nichols were unanimously elected Honorary Members of the Society. The chief public address was given at Convention Hall on Wednesday evening, April 27th, by Charles F. Chandler, on "Chemistry in the United States." At the general meeting on Tuesday afternoon, the following general papers were presented:

General Meeting, Convention Hall, Clinton Avenue South.

E. C. Franklin, "Ammono Carbonic Acids."

C. E. K. Mees, "The Measurement of Color." (Illustrated.)

W. D. Bancroft, "Blue Eyes and Blue Feathers." (Illustrated.)

R. E. Wilson, "Surface Films as Plastic Solids,"

Irving Langmuir, "The Relation between the Stability and the Structure of Molecules."

G. N. Lewis, "Ionization of Electrolytes."

The following Divisions and Sections met: Divisions of Agricultural and Food Chemistry, Biological Chemistry, Dye Chemistry, Chemistry of Medicinal Products, Industrial and Engineering Chemistry, Organic Chemistry, Physical & Inorganic Chemistry, Rubber Chemistry and Water, Sewage and Sanitation; Sections of Cellulose Chemistry, Petroleum Chemistry, and Sugar Chemistry and Technology. Further details of their meetings will be found in the May issue of the *Journal of Industrial and Engineering Chemistry*.

Tuesday evening was given up to dinners and gatherings of various colleges and fraternities. Thursday evening the Good Fellowship Meeting, complimentary to the members by the Rochester Section, consisted of a dinner in the Bausch and Lomb dining hall, followed by a varied and interesting program consisting of music, vaudeville entertainment, motion pictures of the convention itself and prominent members thereof, and a film shown for the first time, picturing the operations of the Eastman Kodak Company. The scientific program was the most extensive ever presented before a meeting of the American Chemical Society and consisted of 280 papers.

CHARLES L. PARSONS, *Secretary*.

## ADVISORY COMMITTEE MINUTES.

The Advisory Committee met at the Hotel Rochester, Rochester, N. Y., Monday, April 25, at 1.30 o'clock, with President Smith and Messrs. Herty, Howe, Lamb, Rosen-garten and Parsons present.

The Committee unanimously voted that in their opinion the Eschenbach Printing Company should be relieved from any penalties incident to a threatened strike of their printers and that the matter be brought before the Council with the recommendation that a similar vote be passed.

It was voted that it was not expedient to send further delegates to the National Trade Council as the Society was not a trade organization.

The question of delegates to the Brussels meeting of the International Union of Pure and Applied Chemistry was discussed and the matter was left to the National Research Council with certain suggestions of members who might be available in Europe at the time.

The Advisory Committee recommended that President Smith nominate E. C. Franklin, John Johnston, and John E. Teeple to succeed themselves in the Division of Chemistry and Chemical Technology of the National Research Council. This was done by President Smith.

The Committee recommended to the President that G. A. Richter be appointed to succeed R. C. Tolman, resigned, on the Committee to Cooperate with the Chemical Warfare Service. This also President Smith approved.

The Advisory Committee voted to recommend to the Council that we reaffirm opposition to the Nolan Patent Bill and the removal of the Federal Trade Commission "rider" therefrom, but that the Society declined to take any position on the so-called Federal Trade Commission "rider" if presented as a separate bill.

The Advisory Committee, after carefully considering the charges against Mr. Charles Bramson and the evidence presented, unanimously recommended that he be expelled from the Society for knowingly and willingly helping to distribute propaganda for the overthrow of our government by force.

CHARLES L. PARSONS, *Secretary*.

## COUNCIL MINUTES.

The Council of the American Chemical Society met at the Hotel Rochester, Rochester, New York, at 4 P. M., Monday, April 25, 1921, with President Edgar F. Smith in the Chair and the following Councilors present:

*Ex-Officio*.—W. D. Bancroft, W. D. Bigelow, E. J. Crane, A. W. Dox, Charles H. Herty, W. F. Hillebrand, John Johnston, Arthur B. Lamb, A. D. Little, Charles L. Parsons, Edgar F. Smith, H. F. Talbot.

*Councilors-at-Large*.—C. L. Alsberg, Edward C. Franklin, Bernhard C. Hesse, H. E. Howe, L. W. Jones, Irving Langmuir, William McPherson, George D. Rosengarten.

*Local Sections*.—*Ames*, W. F. Coover (subs. for J. A. Williamson). *California*, Ralph A. Gould. *Chicago*, D. K. French (subs. for W. R. Smith), W. Lee Lewis (subs. for Julius Stieglitz), Herbert N. McCoy, G. A. Menge (subs. for L. M. Tolman), A. V. H. Mory (subs. for C. S. Miner), L. V. Redman, S. L. Redman (subs. for A. M. Taylor), W. D. Richardson, Gerald L. Wendt (subs. for T. J. Bryan), Frank C. Whitmore (subs. for R. J. Quinn). *Cincinnati*, Hugh M. Campbell (subs. for M. B. Graff), A. B. Davis, C. P. Long, A. P. Mathews. *Cleveland*, O. F. Tower, A. W. Smith. *Colorado*, W. Engle (subs. for S. J. Osborn). *Columbus*, H. D. Higley. *Connecticut Valley*, Jos. S. Chamberlain, C. R. Hoover. *Cornell*, A. W. Browne. *Delaware*, Hamilton Bradshaw, P. B. Holmes (subs. for Charles L. Reese), Roger Williams (subs. for George Norman). *Eastern New York*, E. H. Darby (subs. for Edward Ellery). *Indiana*, F. C. Atkinson, Frank R. Eldred, Edward G. Mahin. *Iowa*, Edward Bartow. *Kansas City*, F. B. Dains. *Lehigh Valley*, Eugene C. Bingham. *Louisiana*, C. E. Coates. *Midland*, William J. Hale. *Minnesota*, A. D. Hirschfelder (subs. for E. P. Harding). *Nebraska*, Fred W. Upson. *New Haven*, Harold Hibbert (subs. for W. R. Hibbard). *New York*, Charles Baskerville, C. A. Browne, Robert P. Fischelis (subs. for F. J. Metzger), Irving Fellner (subs. for J. R. M. Klotz), Ellwood Hendrick, Martin H. Ittner, James Kendall, A. C. Langmuir, K. G. Mackenzie, Ralph H. McKee, R. R. Renshaw (subs. for F. E. Dodge), Charles F. Roth, Wallace Savage (subs. for Ralph G. Wright), H. G. Sidebottom (subs. for D. W. Jayne), B. R. Tunison, John B. Tuttle (subs. for V. C. Edwards), David Wesson. *Northeastern*, George L. Coyle, Winthrop

C. Durfee, George S. Forbes, William A. Kingman (subs. for Robert S. Weston), Robert W. Neff (subs. for W. L. Jennings), James F. Norris, Wm. K. Robbins, Robert E. Wilson (subs. for W. K. Lewis). *Oregon*, O. F. Stafford (subs. for John Fulton). *Philadelphia*, G. E. Barton, A. M. Comey, J. S. Goldbaum, E. H. Grafton (subs. for W. C. Carnell), Walter T. Taggart, James G. Vail. *Pittsburgh*, Alexander Silverman, H. C. P. Weber (subs. for J. O. Handy). *Puget Sound*, Harlan L. Trumbull (subs. for H. K. Benson). *Rochester*, H. T. Clark, Harry LeB. Gray. *South Jersey*, H. Gibbs (subs. for Wm. Kirk). *St. Louis*, Charles E. Caspari, E. Mallinckrodt, Jr., E. J. Sheppard (subs. for L. McMaster). *University of Illinois*, Roger Adams, E. W. Washburn. *University of Michigan*, H. H. Willard. *Virginia*, W. F. Rudd. *Washington, D. C.*, W. D. Collins, R. C. Cook (subs. for W. M. Clark), J. B. Read (subs. for R. B. Sosman), Atherton Seidell, L. I. Shaw (subs. for F. W. Smither). *Western New York*, C. G. Derick, Walter Wallace, A. M. Williamson. *Wisconsin*, Victor Lenher, J. H. Mathews.

The Secretary announced the death of Professor Albert C. Hale, former Secretary of the American Chemical Society, and of Professor J. I. D. Hinds, for many years a Councilor of the Society. The Council rose and stood in silent tribute, and a vote was passed that resolutions be prepared and spread upon the Society minutes in tribute to these members.

The resolutions follow:

"WHEREAS: In the death of Doctor Albert C. Hale, of Brooklyn, N. Y., on April 24, 1921, the members of the American Chemical Society recognize the loss of a valued member and associate;

"Therefore, Be It Resolved:

"1. That as a member of the Society for forty-one years and as an earnest worker in all that related to its success during the period of his active life he will always be held in kindly remembrance.

"2. That the profession of Chemistry has lost in Doctor Hale a representative of high character and standing and especially in his chosen sphere of teaching, to which his whole life was devoted, a worker of distinction.

"3. That in the office of Secretary of the American Chemical Society, which he filled from 1889 to 1903, a critical period in the reorganization and growth of the Society, his services in respect to the two vital features of reorganization, namely: General Meetings and Local Sections, for which he acted as an organizer and general director in matter of detail, his enthusiastic labors and persistence were, in large measure, the secret of success, and that his name is imperishably linked in the history of the Society with these two features.

"4. That the sympathy of the Society is respectfully tendered to the family of Doctor Hale and that a copy of these Resolutions be sent to them by the Secretary."

"WHEREAS: In the death of Professor J. I. D. Hinds, of Nashville, Tenn., on March 4, 1921, the American Chemical Society recognizes the loss of one of its most valued members who has been a member of the Society for thirty years, a member of its Council for twenty years, an inspiring teacher for nearly fifty years, a useful citizen, a delightful friend, and a gentleman of learning and refinement,

"Therefore, Be It Resolved that the American Chemical Society wishes publicly to express its sincere sorrow on the loss of so valued a member and instructs its Secretary to transmit to the wife and daughter of Dr. Hinds, our sincere sympathy and to inform them that we, too, share in their loss."

Doctor George D. Rosengarten was elected to succeed himself for a period of two years as a member of the Committee on National Policy.

It was voted that the Society accept the invitation of the Alabama Section of the American Chemical Society to hold its spring meeting for 1922 in Birmingham, the time of the meeting to be determined by the Advisory Committee.

Doctor E. W. Washburn spoke briefly to the Council regarding the Annual Tables of Constants, informing them that Volume 4 could now be ordered from the Chicago University Press, Chicago, Ill., as published in the *Journal of the American Chemical Society*, and urging the support of individuals therefor.

Charles Bramson, of Joliet, Illinois, having been definitely charged with having taken part willingly and knowingly in the distribution of propaganda issued by the United Communist Party, recommending, among other things, the overthrow of our government by force, and all requirements of the Constitution having been duly met, evidence being presented and Mr. Bramson having been given an opportunity to reply thereto, was, by unanimous vote, expelled from membership in the American Chemical Society.

A petition signed by C. L. Alsberg, W. D. Bancroft, W. D. Bigelow, C. H. Herty, W. F. Hillebrand, A. B. Lamb, R. B. Moore, C. E. Munroe, C. L. Parsons, G. D. Rosengarten, and Edgar F. Smith, recommending for Honorary Membership in the American Chemical Society Charles F. Chandler and William H. Nichols, was presented to the Council. The Council unanimously recommended to the General Society their election as Honorary Members, and, as required by the Constitution, this recommendation was signed by a majority of the Council.

In regard to a communication from Edward Ellery, of the Eastern New York Section of the American Chemical Society, recommending that the Council pass resolutions favoring more universal teaching of the German language in our schools and colleges, the Council felt that so long as the technical state of war existed between this country and Germany it would be better to take no action, although realizing fully the importance of the German language to chemists.

H. E. Howe, representing Julius Stieglitz on the International Commission on Critical Tables of Physical and Chemical Constants, reported that 50% of the proposed budget had been raised and that rapid progress was being made.

The Council voted:

That this Council expresses to the Directors of the Society the hope that the Eschenbach Printing Company will be released from any forfeits that may arise under the terms of its contract in connection with the impending strike, due to the insistence upon the 44-hour week, and

That the members of this Council also express their full willingness, in the event such a strike is not amicably settled, to await indefinitely for the publication of the journals of the Society.

The Council voted that the Advisory Committee, on behalf of the American Chemical Society, select the two names to be presented to the Perkin Medal Committee as the American Chemical Society's candidates for the Perkin Medal.

A section of the American Chemical Society to be known as the Arkansas Section was established by the Council, with territory covering the State of Arkansas and with headquarters at Fayetteville, Arkansas, on petition signed by twenty-one members of the Society in good standing in that State.

The Secretary presented a communication to the Council from Raymond F. Bacon, Director of the Mellon Institute, calling attention to the very difficult situation existing throughout the country, not only in the national, but in the state legislatures, regarding the industrial alcohol situation, and particularly alcohol used in the flavoring extract, pharmaceutical and chemical industries. He presented the case as serious, much of the legislation quite unwillingly and apparently unknowingly bringing such hardships to bear upon these industries as to destroy them if enforced. The whole difficulty is due to ignorance on the part of the people presenting the laws, as they are not in a position to

differentiate adequately and intelligently between beverage alcohol preparations and alcohol for necessary manufacturing purposes.

The Council voted that the President should appoint a Committee on Industrial Alcohol to represent the Society in this matter and to formulate resolutions to be presented by them to the National and the State Legislatures concerned, in order to insure action which will protect the legitimate industries using alcohol and to properly distinguish between prohibition enforcements and the regulation of alcohol for industrial purposes.

It was further voted that any resolutions or recommendations of this kind which they may propose, when unanimously approved by the Committee on National Policy, shall become the action of the American Chemical Society.

The Council also asked Dr. Bacon to present the matter before the General Meeting on Tuesday morning, April 26th, which was done.

The President appointed Martin H. Ittner, Chairman, R. F. Bacon, Chas. Baskerville, F. R. Eldred, Edward Mallinckrodt, Jr., Geo. D. Rosengarten, and B. R. Tunison as the Committee.

The following resolutions were later adopted, and, being unanimously approved by the Advisory Committee, have, by the above vote of the Council, become the action of the American Chemical Society:

WHEREAS, the use of alcohol in many important industries is absolutely necessary not only to the continuance of such industries, but also for the manufacture of articles needed by other industries and even for the production of articles necessary to the protection of and sustenance of life itself, and

WHEREAS, it is the policy expressed in the National Prohibition Act to encourage the use of industrial alcohol for non-beverage purposes, such as the manufacture of thousands of necessary medicinals and countless dyes, chemicals, and perfumes and for the production of heat, light and power,

*Be It Resolved*, that the American Chemical Society advises and most strongly urges for the national welfare that all legislation for the enforcement of prohibition be so clearly drawn as not to restrict the activities of legitimate industries which must have industrial alcohol, and that all such legislation be so drawn as to provide in specific sections for the encouragement of the proper use of alcohol in the industries.

The following amendment to Article XI of the Constitution of the American Chemical Society was proposed to take effect beginning with the financial year of 1921.

Article XI shall be amended to read:

Section 1. The apportionment of funds to Local Sections shall be upon a sliding scale based upon their total paid membership of the year preceding, as follows:

Sections having less than 50 members, not exceeding \$2.25 per member; provided that a minimum of \$75.00 be allowed any Section.

Sections having not less than 50 members nor more than 125, not exceeding \$2.00 per member.

Sections having not less than 125 members nor more than 200, not exceeding \$1.50 per member.

Any Section having 200 or more members, not exceeding \$1.25 per member.

Provided that any Section may claim, etc.

Signed by: A. M. Comey, G. E. Barton, D. K. French, Harry LeB. Gray, James F. Norris, C. G. Derick, William J. Hale, L. I. Shaw, A. Silverman and Wm. W. Wallace, Members of the Council.

As required by the Constitution, a Committee of three was appointed by the President to which this amendment was referred. The Committee is as follows: H. E. Howe, Chairman, H. LeB. Gray, and A. V. H. Mory.

The Council unanimously voted its hearty thanks and appreciation to the Chairmen and members of the local committees of the Rochester Section and to the many in-

dividuals, firms and institutions in Rochester who contributed so bountifully to the success of the meeting.

The following resolution was presented and was unanimously passed by the Council:

WHEREAS, it appears probable that the Congress will speedily enact legislation terminating the state of war, and

WHEREAS, the power of the War Trade Board to control importations of coal-tar chemicals under the Trading-with-the-enemy Act automatically expires with the proclamation of peace, and

WHEREAS, we feel that the need of continued control of such importations from whatever source is urgent,

*Therefore Be It Resolved:*

First, that the Council of the American Chemical Society, representative of a nation-wide membership of fifteen thousand chemists, urge upon both the Senate and the House of Representatives the passage of ad interim legislation which will fully safeguard this industry until the Congress has adopted permanent protective legislation.

Second, that this resolution be telegraphed to the Chairman of the Finance Committee of the Senate and to the chairman of the Ways and Means Committee of the House of Representatives.

Telegrams were sent to the Chairman of the Finance Committee of the Senate and to the Chairman of the Ways and Means Committee of the House of Representatives.

A luncheon to be given to Mme. Curie in New York City on May 15th at the Hotel Waldorf was announced, and the attendance of members was urged.

The Committee appointed by the Council at Chicago to arrange for a longer time for the reading of scientific papers at general meetings reported that they recommended not less than four half days be devoted to divisional meetings at the general meetings of the Society. This recommendation was adopted.

The following resolution was presented and unanimously adopted:

WHEREAS, special knowledge is required in examining chemical patents and in making searches relating thereto, therefore be it

*Resolved:* that the Secretary of the American Chemical Society be authorized to call the attention of the Commissioner of Patents to the facts and recommend to him that a chemically trained examiner be appointed upon his staff of chief examiners.

The following resolution was presented and unanimously adopted:

*Resolved:*

The Secretary of each Division and Section of the Society is hereby authorized to demand submittal in advance of any paper offered for the program of a General Meeting, for decision as to its suitability for presentation at a General Meeting. The chairman and secretary of each Division and Section, acting jointly, are hereby authorized to decline acceptance of any paper, if in their judgment the circumstances warrant such action.

The Secretary presented to the Council a statement of the effect the change of dues had on the membership, showing that to date the Society was approximately nine hundred paid members behind the corresponding date of last year, but that the reason for this drop-off was unquestionably also due to the industrial depression as well as to the increase of dues. Of the fifteen thousand members, up to the present time one thousand one hundred and seventeen have availed themselves of the 33 1/3% discount as being registered undergraduate or post-graduate students in chemistry in some educational institution.

Mr. T. G. Delbridge, delegate of the Society to the meeting of the American Petroleum Institute in New York on April 17th, presented a report, which will be found printed in the May issue of the *Journal of Industrial and Engineering Chemistry*.

*The Committee to Coöperate with the Chemical Warfare Service* reported and its report will be found in the May issue of the *Journal of Industrial and Engineering Chemistry*.

*The Committee on Coöperation between Industries and Universities* reported progress and suggested the appointment of an entirely new committee which should be smaller in number but relatively larger representation from the industries.



*The Endowment Committee* reported that owing to the economic conditions the Committee had made no attempt to secure contributions or pledges to the endowment fund of the Society.

*The Committee on Exchanges* reported that the Society has now 355 exchanges; that during the year 69 new exchanges had been arranged, 11 old exchanges interrupted for one reason or another had been resumed, 4 exchanges discontinued, 7 offers to exchange refused. A list of new exchanges accompanied their list.

*The Committee on Guaranteed Reagents and Standard Apparatus* made an interesting report, which will be found printed in the May issue of the *Journal of Industrial and Engineering Chemistry*.

It was voted, in order to expedite the work of the Committee in case they make reports between meetings of the Council, that the Advisory Committee be empowered, when unanimous, to adopt the report, and when it be adopted that it be considered as the action of this Council.

*The Committee on Institute for Drug Research* presented a report which will be found printed in the May issue of the *Journal of Industrial and Engineering Chemistry*.

*The Insulation Committee (to Coöperate with Engineering Division, National Research Council)* reported progress.

*The Committee on International Normal Weight for Saccharimetric Sugar Solutions* reported that it appeared to be impossible to hope for the adoption of an international normal weight until international relationships became more settled.

*The Membership Committee* reported that during the year 2,289 individual members had been elected, also 75 corporate members and two life members; that 625 members had been dropped for delinquency, 591 had resigned, 53 had died, and that the total membership on December 31, 1920, was 15,582.

*The Metric System Committee to Coöperate with the American Metric Association, World Trade Club, London and Manchester Metric Associations* presented its report, which was discussed at some length and slightly modified. The modified report, as adopted by the Council, will be found in the May issue of the *Journal of Industrial and Engineering Chemistry*.

*The Committee on Morris Loeb Museum* reported as follows:

Your committee has been informed that such portion of the income of the Loeb bequest as is available for expenditure was turned over to the Smithsonian Institution in December last. The matter of the transfer of other property purchased by the Loeb funds consisting of one storage case, storage receptacles, a museum case, index cards and other stationery was taken up jointly by your committee and the officials of the Smithsonian Institution with the Chemists' Club in New York City with a view to having it transported to the Smithsonian Institution in Washington. Only a part of this material has been shipped to the Smithsonian Institution, the storage case at the date of writing not yet having been received. Until all this property is in the hands of the Smithsonian Institution, that Institution is not in position to take care of the materials collected without expending any of the fund for fresh storage cases and there was little occasion for your committee to function. Plans for building up the museum and for taking care of the material have been made in a tentative way. It is hoped the transfer of the property may soon be completed when your committee, if continued, will actively coöperate with the Smithsonian Institution in building up the museum.

C. L. ALSBERG, *Chairman*.

*The Committee on Nomenclature, Spelling and Pronunciation* reported as follows:

Work towards the standardization of chemical nomenclature and spelling in this country and Great Britain has progressed slowly during the past year. Tentative rules covering the more important points have been agreed upon and submitted to the corresponding committee of the London Chemical Society and to that of the Society of Chemical Industry. The latter committee has not thus far sent word of any action but the former committee has written us that it is in substantial agreement with the rules approved by our committee. A few minor changes were suggested and are under consideration.

The chairman of your committee receives rather frequent requests for information regarding points of nomenclature and spelling and gives such advice as he is able to send, pending the adoption of official rules. It is not practicable for your committee, which is a large one, to consider separately every little inquiry which is received. It is the purpose first to establish general principles and to consider only the more important specific points. I am careful to make it clear that advice offered from our experience in connection with *Chemical Abstracts* is not an official opinion of the committee. It seems best to try to help as much as we can even in an unofficial way.

Efforts are being made, particularly by the E. I. du Pont de Nemours & Co., to improve chemical nomenclature in trade usage. A discussion of this was published in the *Journal of Industrial and Engineering Chemistry*, 12, 1026. Your committee, through its chairman, has coöperated in this movement by conference and correspondence.

The chairman is also coöperating in the work of the Sub-Committee on Nomenclature of the U. S. Pharmacopeia Revision Committee, an appointment to which sub-committee he has accepted.

Respectfully submitted,

E. J. CRANE, Chairman.

*The Committee on Occupational Diseases in Chemical Trades* made an interesting and extensive report, which will be found printed in the May issue of the *Journal of Industrial and Engineering Chemistry*.

*The Paper Committee* reported that the quality of the present paper of the journals was far below the pre-war standard and recommended that as soon as possible the paper be brought back to the regular standard paper of the Society.

*The Patent and Related Legislation Committee* reported as follows:

The Patent and Related Legislation Committee begs to submit the following annual report:

During the past year your Committee has very actively continued its efforts to aid in securing the enactment of legislation for the relief of the Patent Office and to make certain beneficial changes in the Patent Statute, measures for which were embodied in Nolan Patent Office Bill H. R. 11,984.

The next event in these activities of your Committee, following its report of March 22, 1920, the bill having passed the House of Representatives in satisfactory form, was an extended hearing, beginning on April 8, 1920, before the Senate Committee on Patents, on the salaries, force, and damages features of the bill. The personnel of your Committee and of the Society took an active part in this hearing. The chairman of your committee on Patents and Related Legislation made an address before the Senate Patent Committee and introduced a resolution of the Society in favor of the Patent Office bill. The Secretary of the Society, Dr. Charles L. Parsons, appeared at the hearing to represent the Society and seven members of the Society were also present. A stenographic report of the hearings is attached hereto. Although there was a very large delegation present and the Senate Committee seemed to be convinced of the need of passing the bill, substantially as it had come from the House of Representatives, except for some amendments to the provision for fixing damages for infringement, your Committee was greatly surprised and disappointed to find that the Senate Committee reported the bill with what is known as the Federal Trade Commission section attached thereto. This section was intended to give the Federal Trade Commission power to receive and administer inventions and patents of Government employees. It had not been considered at the hearing, and the only justification for attaching it to the Nolan Bill was that it had once passed the Senate and that it would enable the House of Representatives to consider such section with the patent office relief and damages section in a single bill.

It was also necessary in the Senate to have unanimous consent in order that the bill might be brought up before the adjournment of the session. The Chairman of the Appropriations Committee so vigorously opposed the bill that in order to remove his objection to unanimous consent, the Chairman of the Patents Committee of the Senate consented to amendments to the numbers and salaries of the examiners, which emasculated the bill and made it in some respects worse than the present law.

The bill was sent to a Conference Committee, comprising members of both the Senate and House.

The Federal Trade Commission Section had had hearings before the two Patent Committees of Congress, but only those in favor of the bill appeared at the hearings. When the said section was attached to the Nolan Patent Office Bill, it received the attention of many who had not seriously considered it before, and many very strenuous opponents to the section appeared. In view of this, the Conference Committee, contrary to the usual custom, held a hearing on the Federal Trade Commission section for two days in January, 1921. Your Committee presented a resolution of the American Chemical Society urging the Conference Committee to eliminate the Federal Trade Commission section from the bill, in order that the Patent Office relief might not be delayed or prevented from becoming a law by the presence of the said section. Your Committee also took the opportunity to vigorously urge the need of immediate relief for the Patent Office, although the Conference Committee did not invite dis-

cussion of that subject. The Conference Committee reported the bill with the Federal Trade Commission section modified but retained therein, restored the figures for the salaries and numbers of examiners to the condition in which they passed the House of Representatives, and made amendments to the damages section, so that it avoided all the objections raised against it, except that it was a mere codification of the law embodied in the decisions of the courts, which objection is not founded on fact.

The Chairman of your Committee, with representatives of other organizations, went to the Chairman of the Committee on Rules of the House of Representatives and secured the promise of a rule giving the Conference report almost immediate right of way in the House of Representatives. The House promptly voted to approve the Conference report, although, because of objection to the Federal Trade Commission section the majority vote was not large, as it had been when the bill first passed the House without that section.

Because of opposition to the Federal Trade Commission section and the threat that the bill would be talked to death in the Senate on account of the said section, if brought to a vote, the Chairman of the Patent Committee of the Senate did not bring the bill to a vote, and it died with the expiration of the 66th Congress, March 4, 1921.

The Chairman of your Committee spent the last two days of Congress in Washington, seeking to reconcile the opponents of the bill, so that the Patent Office might get its relief, but without success.

A draft of a proposed report, dated March 11, 1921, of your Committee, urging that the Society should oppose the enactment of the Federal Trade Commission section, either as a part of the Patent Office Bill or as a separate bill, and recommending that the Committee on National Policy request each member of the American Chemical Society to write the Committeemen and Members of Congress, urging them to secure the elimination of the Federal Trade Commission section from the bill and the immediate introduction and passage of the bill, and also to prevent the Federal Trade Commission section from becoming a law, even as a separate bill, was sent to the members of the Patent and Related Legislation Committee for vote. As three of the Committee approved of the three recommendations in the report: First, removal of the Federal Trade Commission section from the bill; Second, the immediate introduction and passage of the bill; and Third, that the Federal Trade Commission section should be opposed upon its merits and prevented from becoming a law, and only one member opposing the third recommendation, the remaining member not voting on said third recommendation, the said report was forwarded to the Secretary of the Society, with the request that he bring the report to the attention of the Committee on National Policy and of the Council of the Society for action thereon.

The new Chairman of the Patent Committee of the House of Representatives has re-introduced the Nolan Bill, which was Nolan Patent Office Bill, H. R. 11,984, omitting the Federal Trade Commission section, and the new bill will be known as Lampert Patent Office Bill, H. R. 210. Your Committee is already at work endeavoring to secure the passage of this bill.

Another patent bill has also had the attention of your Committee during the last few weeks of the 66th Congress, namely, Nolan Treaty Patent Bill, H. R. 15,662, which extended the time for filing and prosecuting applications for patents in the United States Patent Office. The reason for this bill was the following:

The International Convention of Paris, of March 20, 1883, to which the United States is a party, provides that if an inventor shall file his applications for patents in any of the Treaty Countries foreign to him within one year after his application has been filed in his own country, then the said foreign applications shall be given the same effect in contest with other inventors and in overcoming alleged prior public uses as if the said foreign applications had been filed simultaneously with the one in his own country; and as the war has prevented many inventors from filing applications in countries foreign to their own within the said one year after their domestic applications, the Peace Treaty and the Berne Convention of June 30, 1920, have extended the time within which to file such applications and to pay fees and take other steps in the prosecution of such applications which were filed or would have been filed during the war without loss of rights; and as many hundreds of applications have been filed and belated fees paid by American citizens in European countries which are parties to said latter Convention and have been accepted by those countries on the supposition that the United States would pass reciprocal legislation; and as the failure to pass such legislation would result in the invalidation of all such applications and payments of fees, Nolan Bill, H. R. 15,662 was introduced for this purpose. This bill protects American citizens from undue effect of filing of applications for patent here by foreign inventors, by reserving a license under any patent granted or validated by reason of the said act to an American citizen, who, before the passage of the act, was *bona fide* in possession of any rights in patents or applications for patents which conflict with any of said patents, and also by preserving to any citizen of the United States, his agent or successors in business, the right to continue any manufacture, use of sale commenced before the passage of such act by such citizen, even though such manufacture, use or sale might infringe a patent granted or validated by reason of the act.

Your Committee was compelled, during the closing days of the Session of Congress, to aid in the passage of this bill, and prepared a resolution in favor of the bill, which was approved by a majority of

the members of your Committee (all who voted), and was forwarded to the Secretary for action by the Public Relations Committee. Before such action could be obtained, the bill was passed both by the Senate and House and became a law.

Respectfully submitted,

EDWIN J. PRINDLE, *Chairman*, Patent and Related Legislation Committee,  
American Chemical Society.

When this report was presented by the Secretary, it was voted that the Society reaffirms its position as to the Nolan Bill and the removal of the Federal Trade Commission "rider" therefrom. Later in these proceedings will be found a second vote placing the Society on record as opposed to the so-called Federal Trade Commission "rider" either as a rider or as a separate bill.

*The Committee on Platinum Theft Control* reported a careful consideration of possible means to decrease the thefts of platinum; that they had done everything they could to make public all data regarding such thefts and had taken up with members of Congress the question of presenting a bill to Congress covering a scheme for licensing platinum refiners, so that all refining would have to be done by firms properly licensed by the United States government, and that this would be given further consideration.

*The Priestley Memorial Committee* reported that the sum of Two Thousand Dollars had been collected and placed on interest; that the Committee had authorized the Chairman to select an artist to copy the Stuart portrait of Priestley, which is now at Northumberland, Pa., and that immediate steps would be taken to obtain a die for the Priestley medal.

*The Committee on the Revision of Methods of Coal Sampling and Analysis (Joint with the Society for Testing Materials)* asked to be continued another year as further tests of an alternate method have not been completed and the tentative method will probably be continued for another year.

*The Committee on Supervision of Chemical Engineering Catalog* reported and the report will be found printed in the May issue of the *Journal of Industrial Engineering and Chemistry*.

*The Supervisory Committee on Standard Methods of Analysis* reported as follows:

The only report acted upon by the Supervisory Committee is that from the Committee on Cottonseed Products, of the Division of Industrial and Engineering Chemists, which was published in the *Journal of Industrial and Engineering Chemistry*, 12, 707, 1920.

A report of the Fusibility of Coal Ash from the Committee on Coal Sampling and Analysis, a joint committee with one from the American Society for Testing Materials, was approved subject to final action by the American Society for Testing Materials, which has published it as tentative. If modified in any way, the report will be again submitted to the Supervisory Committee.

Respectfully submitted,

W. F. HILLEBRAND, *Chairman*, Committee on Standard Methods of Chemical Analysis.

*The World Metric Standardization Committee* reported that the Committee had been active during the year in endeavoring to secure legislation for the introduction of the Metric System in America.

*The Committee on Standard Methods for the Examination of Water and Sewage to Coöperate with the Committee of the American Public Health Association* reported as follows:

The committee met at the call of Mr. W. F. Monfort, chairman of the American Public Health Association committee, at the University of Chicago, December 28-29, at which time the questions with regard to standard methods were discussed in general, and in accordance with the policy of the American Public Health Association, questions were referred to referees as follows:

E. M. CHAMOT, chlorine; nitrates.

W. D. COLLINS, mineral analysis; standard specifications for Nessler tubes; turbidity.

R. E. GREENFIELD, dissolved gases and total hardness.

- H. B. HOMMON, sewage testing methods.  
 H. E. JORDAN, analysis of chemicals used in water treatment.  
 F. W. MOHLMAN, methods for testing sewage.  
 E. B. PHELPS, ammonia in water and sewage.  
 A. M. BUSWELL, definition of alkalinity and temporary hardness.

Respectfully submitted,

A. M. BUSWELL, *Chairman*, American Chemical Society Coöperative Committee.

The Committees appointed by President Smith for the ensuing year will be found on the third page of Proceedings, this issue.

Following the Committee Reports the report of the Patent and Related Legislation Committee was again taken up and after extended discussion the following motion was passed by a vote of 59 in favor, 24 opposed, and 12 not voting:

Moved that the Council of the American Chemical Society go on record as opposed to the substance of Section 9 of the Nolan Bill, H. R. 11984 of the 66th Congress, 3rd Session.

Dr. Charles Baskerville as representative of the Society to the meeting of the American Mining Congress in the Old Colony Club, Biltmore Hotel, March 10, 1921, reported that he was present and took part in the proceedings, and that the Congress had important plans in view for gathering together of data and formulating a plan to assist the Secretary of Commerce.

Dr. Charles Baskerville, the Society's representative in the Holmes Memorial Safety Association, reported that the Association was functioning actively; that the Society had been represented at meetings of the Association, at which local chapters of the Holmes Safety Association were authorized throughout the United States to aid and promote among mine workers and companies a movement for first aid, safety and sanitation.

CHARLES L. PARSONS, *Secretary*.

#### MEMBERS ELECTED APRIL 15TH-MAY 15TH.

- Alker, Charles H., 155 Thomas St., Bloomfield, N. J.  
 Asuncion, Silvestre, Box 204, Univ. Station, Baton Rouge, La.  
 Baldwin, George H., Oleum, Cal.  
 Beguiristain, G., Box 376, University, Va.  
 Bernhard, Hermann, 147 W. 103rd St., New York City.  
 Bersey, John Mack, 61 Broadway, New York City.  
 Binns, Frederick Walter, 1043 Tremont St., Boston, Mass.  
 Brossman, Philip D., 228 W. Clapier St., Germantown, Philadelphia, Pa.  
 Brown, Rachel F., 5707 Kenwood Ave., Chicago, Ill.  
 Buhrig, Wm., Fleischmann Yeast Co., Langdon, Washington, D. C.  
 Burkhart, Clarence W., 37 Liberty Ave., Dongon Hills, S. I., N. Y.  
 Chidlow, David, Ridgefield, Conn.  
 Coburn, Stuart E., 14 Beacon St., Boston, Mass.  
 Cole, F. N., Box 401, Grinnell, Iowa.  
 Christmann, Philip S., 700-704 W. Division Street., Chicago, Ill.  
 Darke, Wilfred F., Christopher Thomas & Bros., Ltd., Broad Plain Works, Bristol, England.  
 Davis, T. A., 635 Eye St., S. E., Washington, D. C.  
 Davison, Forrest R., 1109 13th Ave., S. E., Minneapolis, Minn.  
 Edwards, Edwards, 103 Ashfield St., Piedmont, W. Va.  
 Fellner, Irving S., 50 Oakland St., near Vale Place, Rye, N. Y.  
 Frank, George C., Jr., 400 34th St., Norfolk, Va.  
 Gleditsch, Ellen, Universitets Kemiske Laboratorium, Kristiania, Norway.  
 Hardin, George H., 80 South St., New York City.  
 Harkness, H. S., Crockett, Cal.  
 Harrel, C. G., Liberty, Mo.  
 Herzog, Max A., 539 St. Louis St., Springfield, Mo.  
 Hull, John D., 143 Morley Ave., W., Dearborn, Mich.  
 Isern, Elmer H., 1614 Kentucky St., Lawrence, Kans.  
 Jayne, Earl H., Webster, N. Y.  
 Jecusel, Frederick Paul, Chatham Rubber Co., Portland, Conn.  
 Kaefer, C., 1146 22nd St., Milwaukee, Wis.

- Kell, Sherman L., 1424 Bryn Mawr Ave., Chicago, Ill.  
 Kennard, Edward M., 325 Ilchester Ave., Baltimore, Md.  
 Lacey, George W., 1049 S. Ave., Rochester, N. Y.  
 Lahman, Clifford K., 611 South 7th St., Springfield, Ill.  
 Lasher, F. G., 124 Moffatt St., Brooklyn, N. Y.  
 Leach, Lester C., 53 Beech St., Framingham, Mass.  
 Leeder, George B., Foot of Howell St., Chester, Pa.  
 Lilly, Louise (Miss), 3300 Woodford Road, Cincinnati, Ohio.  
 Line, William, York St., Sackville, N. B., Canada.  
 Lowry, Earl M., Steele Hall, Syracuse Univ., Syracuse, N. Y.  
 Ludwig, August, 1407 State St., Menominee, Mich.  
 Miller, Lewis, Parkersburg, Iowa.  
 Olander, C. P., 3233 Campbell, Kansas City, Mo.  
 Owen, Benton B., University, Va.  
 Padhye, Ramchandra Govind, Louisiana State University, Department of Chemistry, Baton Rouge, La.  
 Parrish, Geo. J., S. P. E. House, University, Pa.  
 Pearson, Elmer A., 513 Washington Ave., S. E., Minneapolis, Minn.  
 Perkins, G. Richard, 38 Huntington St., Hartford, Conn.  
 Petersen, Julius, Solvgade 83, Copenhagen, Denmark.  
 Pontecorvo, Louis, 2053 First Ave., New York City.  
 Redmond, Allyn C., 245 Steuben St., Brooklyn, N. Y.  
 Rhoads, Evan L., 81 Haddon Ave., Haddonfield, N. J.  
 Ritchie, C. Kenneth M., Mellon Institute, Pittsburgh, Pa.  
 Roberts, Benjamin W., 110 North Front St., Philadelphia, Pa.  
 Robinson, L. K., 5435 Kimbark Ave., Chicago, Ill.  
 Sanders, Elmer N., 43 Byfield St., Bristol, R. I.  
 Sanders, V. H., 546 Newbury St., Boston, Mass.  
 Sayer, Wynne, Secretary, Sugar Bureau, Imperial Department of Agriculture, in India, Pusa, Bihar, India.  
 Saylor, Charles H., 106 Montgomery St., Poughkeepsie, N. Y.  
 Schumacher, E. E., 341 N. Grove St., East Orange, N. J.  
 Seidensticker, William, 422 So. Cuyler Ave., Oak Park, Ill.  
 Sengson, Pedro T., Box 15, University Station, Baton Rouge, La.  
 Smith, Charles E., Vacuum Oil Company, 61 Broadway, New York City.  
 Snider, Ellwood H., 20 Normandy Ave., Rochester, N. Y.  
 Stick, Edward Moyle, 5 Devon Row, St. Johns, Newfoundland, Canada.  
 Taub, Abraham, Columbia College of Pharmacy, 115 W. 68th St., New York City.  
 Thomas, Robert W., 319 Dryden Road, Ithaca, N. Y.  
 Wallfred, C. L., 4550 Wentworth Ave., So., Minneapolis, Minn.  
 Weinstein, Samuel, 1 Auburn Ave., Richmond, Va.  
 Williams, Filix N., Sachern Head, Guilford, Conn.  
 Wilson, Malvern, 262 W. Washington St., Nelsonville, Ohio.  
 Witherspoon, Robert, 5048 Chichester Ave., Jamaica, L. I., N. Y.  
 Wyman, Le Roy L., 713 7th Ave., S. E., Minneapolis, Minn.

## CORPORATION MEMBERSHIPS.

- Alpha Portland Cement Co., Easton, Pa.  
 The Appleton Coated Paper Co., Appleton, Wis.  
 Baker & Co., Inc., 54 Austin St., New York City.  
 Eaton Co., Ltd., The, % Research Chem. Lab., Toronto, Canada.  
 Gallun & Sons Co., A. F., Milwaukee, Wis.  
 Gaskill Chemical Corporation, 157 Spencer St., Brooklyn, N. Y.  
 Higgins & Co., Chas. M., 271 9th St., Brooklyn, N. Y.  
 Hub Dyestuff & Chemical Co., 595 East Seventh St., Boston, 27, Mass.  
 Lever Brothers Co., Cambridge, Mass.  
 Mellin's Food Co. of N. A., 177 State St., Boston, Mass.  
 Merrimac Chemical Co., Research Dept., Woburn, Mass.  
 Murray Co., Edgar A., 2703 Guain St., Detroit, Mich.  
 Oakley Chemical Co., 22 Thames St., New York City.  
 Parke, Davis & Co., Detroit, Mich.  
 Pfister & Vogel Leather Co., Milwaukee, Wis.  
 Pouvallsmith Corporation, Smith St., Poughkeepsie, N. Y.  
 Reading Extract Co., Inc., 307 Little Grape St., Reading, Pa.

Rosemont Dyeing Co., Woonsocket, R. I.  
 Scott & Co., Henry L., 101 Blackstone St., Providence, R. I.  
 Stecher Lithographic Co., 274 W. Goodman St., Rochester, N. Y.  
 Sterns, Ltd., Attention L. Chas. Wallach, Managing Director, Royal London House, Finsbury Square, London, E. C. 2, England.  
 Texas Gulf Sulphur Co., 50 East 42nd St., New York City.  
 Waltke & Co., Wm., Second & E. Grand St., St. Louis, Mo.  
 West End Chemical Co., 10th Floor Syndicate Bldg., Oakland, Cal.

## MEETINGS OF SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

### CALIFORNIA SECTION.

The 123rd regular meeting of the Section was held on April 15, when Arthur Lachman addressed the members on "Molecular Rearrangements in Nitrogen Compounds."

The 124th regular meeting occurred on May 7, the evening being devoted to a program arranged by the women chemists of the Section. The following program was rendered: "Introductory Remarks," by Agnes Fay Morgan, of the University of California; "Blood Regeneration as Influenced by Dietary Factors," by Freda S. Robbins, of the Hooper Foundation for Medical Research; and "By-Products of Research in Organic Chemistry," by Hester E. H. Branch, Graduate Student, Department of Chemistry, University of California.

LLOYD W. CHAPMAN, *Secretary*.

### CHICAGO SECTION.

At the regular meeting of the Section, held on April 22, J. H. Mathews, of the University of Wisconsin, spoke on the subject of "Photochemistry."

S. I. REDMAN, *Secretary*.

### CONNECTICUT VALLEY SECTION.

The last meeting of the season was held at Westfield, Mass., on May 21. George C. Whipple, of the Harvard Engineering School, Cambridge, Mass., spoke on "Water Purification."

HARRY WESSELS, *Secretary*.

### DETROIT SECTION.

The 125th meeting of the Section occurred on May 18 when H. M. Pier, of the Research Corporation, New York City, gave a lecture on the Cottrell Precipitation Process.

WM. B. TEMPLETON, *Secretary*.

### INDIANA SECTION.

The Section held its regular monthly meeting on May 14, at Lafayette, Ind. William Hoskins, of Chicago, spoke on the subject, "The Genesis of an Industry."

EDGAR B. CARTER, *Secretary*.

### IOWA SECTION.

A joint meeting of the Ames and Iowa Sections was held on April 29 and 30, at Indianola, Ia., in connection with the meeting of the Iowa Academy of Science. The following program was given: "Further Work in the Study of Free Energy of Aqueous Solutions," by J. N. Pearce and H. B. Hart, of the State University of Iowa; "The Effect of Relative Positions of the Hydroxide and Amino Radicals in the Migration of Acyl from Nitrogen to Oxygen," by L. Charles Raiford and H. A. Iddles, State University of Iowa; and "A Chemical Study of Dolomites," by Nicholas Knight, Cornell College.

L. CHARLES RAIFORD, *Secretary*.

## KANSAS CITY SECTION.

On April 20, the Kansas City Section joined the Engineering School at Lawrence, Kansas, in celebrating the 30th anniversary of the founding of the school as a separate branch.

LEE E. CLARKE, *Secretary*.

## LEHIGH VALLEY SECTION.

On May 5, the Lehigh Valley Section met at Easton, Pa., when C. O. Brown, of the Semet-Solvay Co., Syracuse, N. Y., gave an address on the "Application of Research to the Coal and Coke Industry."

J. G. SMULL, *Secretary*.

## LEXINGTON SECTION.

The 70th meeting of the Section was held on April 20. A paper, by Edwin J. Gott and John B. Nelson, on the subject, "The Work and Purpose of the Bacteriological Division of the Department of Public Service Laboratories," was read.

S. D. AVERITT, *Secretary*.

## LOUISVILLE SECTION.

At the regular monthly meeting of the Section, on April 15, Otto Eisenschimal, of Chicago, gave a talk on "The Chemist as a Business Man."

C. E. GEIGER, JR., *Secretary*.

## MAINE SECTION.

On April 14, E. H. Winslow, of Portland, Me., addressed the members of the Section on "The Manufacture and Uses of Acid Resisting Clay Products."

L. J. WALDBAUER, *Secretary*.

## MARYLAND SECTION.

The 50th meeting of the Section was held on April 22. J. C. W. Frazer, of the Johns Hopkins University, spoke on "The Catalytic Oxidation of Carbon Monoxide," and Niel E. Gordon, of the University of Maryland, gave an address on the subject, "The Hydrogen Electrode and Its Application." Attendance, 30%.

On Sunday, April 24, a meeting was held in memory of the late Prof. H. N. Morse, of Johns Hopkins University, when prominent scientists paid high tribute to the memory of Professor Morse.

C. C. HOWES, *Secretary*.

## MICHIGAN AGRICULTURAL COLLEGE SECTION.

On March 15, R. L. Kahn, of the Michigan Department of Health, spoke before the Section on the subject, "Some Recent Immunological Studies."

At a meeting, held on April 12, H. C. Young, of the Michigan Agricultural College, addressed the members of the Section on "Vitamines in Relation to Plant Life."

W. G. Smeaton, of the University of Michigan, spoke to the members on May 6, taking as his subject, "Chemical Revolution Effected by Lavoisier and the Early Development of Modern Chemistry."

On May 10, Frank Schaffer, of the Laboratory Apparatus Company, Ann Arbor, Mich., gave a demonstration in glass blowing before the Section.

C. S. ROBINSON, *Secretary*.

## MIDLAND SECTION.

At the regular meeting of the Section, held on April 25, N. W. Haynes spoke on "The Tariff Situation."

C. C. KENNEDY, *Secretary*.

## MILWAUKEE SECTION.

Glen Pickard, of the Pickard Research Laboratories, Chicago, Ill., addressed the Section on April 15 taking as his subject, "The Manufacture of Vegetable Oils."



The section held a joint meeting with the American Society of Steel Treaters on May 9. H. F. Moore, of the University of Illinois, spoke on the "Fatigue of Metals."

O. A. CHERRY, *Secretary*.

#### MINNESOTA SECTION.

R. A. Gortner addressed the March meeting of the Section, speaking on the subject "Colloid Problems in Baking."

L. M. HENDERSON, *Secretary*.

#### NASHVILLE SECTION.

The 73rd meeting of the Section occurred on May 6. The following papers were read: "New Developments in the Tennessee Dairy Industry," by Lucius P. Brown; "Sanitary Principles in Milk Production," by Kary C. Davis; "Possibilities of Sweet Potato Syrup Manufacture in Tennessee," by R. E. Kremers; and "Report from the Rochester Meeting," by George L. Clark. In addition to the above program, a reel of motion pictures on "Condensed Milk" was run.

The following officers have been elected for the coming year: J. M. Breckenridge, *Chairman*; J. W. Sample, *Vice-Chairman*; H. A. Webb, *Secretary-Treasurer*, and Lucius P. Brown, *Councilor*.

H. A. WEBB, *Secretary*.

#### NEBRASKA SECTION.

On March 24, H. C. Russell, of the University of Nebraska, addressed the members of the Local Section on "The Acidity of Different Soils."

At the regular meeting of the Section, held on April 11, E. C. Franklin, of Leland Stanford Jr. University, spoke on "Liquid Ammonia and the Ammonia System of Acids, Bases and Salts." Attendance, 50%.

S. B. ARNSEN, *Secretary*.

#### NEW HAVEN SECTION.

The last spring meeting of the Section occurred on May 24, at New Haven, Conn., when Roger Brunel, of Bryn Mawr, lectured on "The Bearing of Recent Theories of Atomic Structure on Organic Chemical Reactions."

BLAIR SAXTON, *Secretary*.

#### NEW YORK SECTION.

A joint meeting of the Local Section, the American Electrochemical Society and Societe de Chimie Industrielle, was held on April 22, at the Chemists' Club. The program was as follows: "Hoist Machinery in Chemical Industry," by E. W. Taylor; "Industrial Trucks and Tractors," by W. P. Kennedy; "Economics in Handling Liquid Coal Tar Products," by S. P. Miller; and "Mechanical Handling of Materials in Large Scale Chemical Operations," by A. E. Marshall.

The annual meeting of the American Section of the Societe de Chimie Industrielle, in joint session with the American Chemical Society, the American Electrochemical Society, and the American Section of the Society of Chemical Industry, was held on May 13, at the Chemists' Club. The following addresses were given: Presiding Officer's address by Marston T. Bogert; "The Industrial Reconstruction in France," by Marcel Knecht, and "The Diamond and Its Industrial Uses," by George F. Kunz.

H. G. SIDEBOTTOM, *Secretary*.

#### NORTH CAROLINA SECTION.

At the Spring Meeting of the Section, held on April 30, at Wake Forest, N. C., the following program was rendered: "*p*-Cymene Studies. II. The Bromination of 2-Amino-*p*-cymene," by Alvin S. Wheeler and Ira W. Smith; "Chlorination with the Silent Electrical Discharge," by Paul Gross; "New Derivatives of 2, 3, 8-Tribromo-5-hydroxy-1, 4-naphthoquinone," by Alvin S. Wheeler and T. M. Andrews; "A Simple

Density Vapor Apparatus," by Paul Gross; "Analysis and Properties of Some Interesting Combustible Compounds," by O. J. Thies, and "A Note on the Minor Test for Dextrose and Tartrates," by G. H. Satterfield.

L. B. RHODES, *Secretary*.

#### NORTHEASTERN SECTION.

The 167th regular meeting of the Section was held on May 20, when the following addresses were given: "Chemistry in a Clothing Store," by Earl B. Millard; "Recent Researches on Coffee, Dehydrated Foods, and Fish." Two reels of moving pictures were exhibited on "Sidelights of the Mammoth Amoskeag Plant," and "Cotton Manufacturing."

L. F. HAMILTON, *Secretary*.

#### PITTSBURGH SECTION.

The 172nd meeting of the Section, held on May 19, was addressed by Dr. Edgar F. Smith, President of the American Chemical Society, on the subject, "A Glance at the Early Inorganic Chemistry of America."

GEBHARD STEGEMAN, *Secretary*.

#### PUGET SOUND SECTION.

On April 27, E. Z. Lynn, of the University of Washington, spoke before the members of the Section on "Some Reactions of Nitroso Compounds."

R. W. ELLISON, *Secretary*.

#### ROCHESTER SECTION.

At the regular meeting of the Section, held on April 18, the following officers were elected: H. T. Clark, *Chairman*; O. I. Chorman, *Vice-Chairman*; E. M. Billings, *Secretary-Treasurer*; J. Ernest Woodland, Ivar N. Hultman and Harry A. Carpenter, *Executive Committee*.

ERLE M. BILLINGS, *Secretary*.

#### SAINT LOUIS SECTION.

A paper entitled, "A New Isomer of Phenolphthalein and Its Properties," was given before the Section on May 2, by L. McMaster and George D. Graves, of Washington University.

H. A. CARLTON, *Secretary*.

#### SOUTHEAST TEXAS SECTION.

At the regular meeting of the Section, on May 12, J. R. Neller, of the Texas Company, spoke on "A Survey of Chemical Research in Agriculture."

P. S. TILSON, *Secretary*.

#### SOUTHERN CALIFORNIA SECTION.

On April 28, J. W. Turrentine, of the United States Department of Agriculture, Bureau of Soils, spoke to the members on the subject, "Chemicals from Kelp."

H. L. PAYNE, *Secretary*.

#### DECEASED.

Briggs, T. Lynton, 188 Central, Flushing, N. Y. Died April 2, 1921.

Pond, G. G., State College, Pa. Died May, 1920.

Sillman, Joseph, 1685 Jos. Campan St., Detroit, Mich. Died February, 1921.

Wette, Francis A., 204 N. Monroe St., Baltimore, Md. Died, 1920.

Willis, A. R., 1471 Irving St., Washington, D. C. Died April 25, 1921.

# Proceedings.

## COUNCIL.

President Smith has appointed Prof. B. B. Boltwood the Society's representative at the inauguration of Dr. James Rowland Angell as president of Yale University on Wednesday, June 22nd.

### MEMBERS ELECTED BETWEEN MAY 15 AND JUNE 15, 1921.

- Ackerman, D. E., 39 Penn Ave., Mansfield, Ohio.  
Adams, W. C., 727 Union Ave., St. Louis, Mo.  
Anderson, Thomas Colby, 412 Camden Court, Ann Arbor, Mich.  
Battermann, A. E., 6619 Wade Park Ave., Cleveland, Ohio.  
Blusievicz, Michael, 1041 Bloomfield St., Hoboken, N. J.  
Brailley, Allen Gilbert, R. F. D. No. 2, Box 57, South Royalton, Vt.  
Brown, Ellis, St. Elmo Hall, University, Va.  
Campbell, Dugald N., Kempthornes Chemical Works, Westfield near Okahuhu, Auckland, New Zealand.  
Cardinaux, Paul, Laval University, Quebec, Canada.  
Chivers, J. H., Electric Alloy Steel Co., Charleroi, Pa.  
Cowgill, George R., 2 Hillhouse Ave., New Haven, Conn.  
Cutter, Harold B., 3 Linncean St., Cambridge 38, Mass.  
Damon, Edmund Ives, 24 Main St., W., Waterloo, N. Y.  
Damon, Sherman, 295 Kent St., Brookline, Mass.  
Davis, Russell H., 9603 Quebec Ave., Cleveland, Ohio  
Denison, George A., Box 268, Faculty Exchange, College Station, Tex.  
Domovs, Sidney, 2848 W. 22nd St., Brooklyn, N. Y.  
Donald, Robert M., 225 W. 18th St., care of N. K. Fairbank Co., Chicago, Ill.  
Duane, Arthur R., 9 Massachusetts Ave., Boston, Mass.  
Duerr, Winslow A., Cornwall-on-Hudson, N. Y.  
Dougall, Stafford R., 156 Nutts Ave., Phoenixville, Pa.  
Elder, Lucius W., Jr., 115 N. Wayne Ave., Wayne, Pa.  
Friedman, William E., 308 Tompkins Ave., Brooklyn, N. Y.  
Gartmann, Peter, Box 67A, R. F. D. No. 1, Orange, Cal.  
Gerard, Harry F., Scripps Biological Institute, La Jolla, Cal.  
Gordon, David, 131 Wildey St., Tarrytown, N. Y.  
Gridley, Stanley T., 1276 Melbourne Road, East Cleveland, Ohio.  
Griffith, Palmer W., Danby, Vt.  
Guerrero, Alberto Lobo, Box 137, Mass. Inst. of Tech., Cambridge 39, Mass.  
Haggenmacher, H. E., 121 W. 74th St., New York City.  
Hall, Wm. McLaurine, Jr., 240 East Broad St., Bethlehem, Pa.  
Hammond, J. M., 828 Lindsey Building, Dayton, Ohio.  
Hance, Francis E., Morse Hall, Ithaca, N. Y.  
Hartsfield, J. D., 533 Main St., Waurika, Okla.  
Hemmi, Fumiwo, P. O. Box 565, Station A, Champaign, Ill.  
Heurich, Vincent Christian, 403 S. 12th St., Lebanon, Pa.  
Hilman, Victor E., Crompton & Knowles Loom Works, Worcester, Mass.  
Hitchcock, Thomas J., Glebe Sugar Refining Co., Ltd., Greenock, Scotland.  
Holland, C. V., Eastville, Va.  
Jewell, Charles Henry, Y. M. C. A. Building, Woonsocket, R. I.  
Jolliffe, Ernest H., 124 Lyndhurst Ave., Toronto, Ont., Canada.  
Just, Julius F., 616½ So. Galena Ave., Freeport, Ill.  
Kampert, George J., 234 N. 16th St., Kansas City, Kans.  
Kennedy, Eugene H., Newark, Del.  
Kenyon, Wm. Houston, Jr., 61 Broadway, New York City.  
Klein, Charles, 87-20 Boulevard, Rockaway Beach, N. Y.  
Koenig, F. Otto, Jr., 1 West 89th St., New York City.  
Krone, Otto August, 4614 S. Grand Ave., St. Louis, Mo.  
Lachman, John H., 73 Oakland St., Red Bank, N. J.  
Lambright, John., 2211 Grandview, Cleveland, Ohio.  
Leonard, C. E., care of C. B. Smith, 36 N. Gift St., Columbus, Ohio.

- Lutz, Robert F., 91 Park St., Newton, Mass.  
 Macormac, Alfred R., 86 Elliott Ave., Tottenville, N. Y.  
 Marks, Frank H., 1002 Fairmont St., Washington, D. C.  
 Marples, Major M. E., 5 Robinson Road, Shanghai, China.  
 McLachlan, John Arthur, 66 8th Ave., Bezendehart Valley, Johannesburg, South Africa.  
 Mudd, Stuart, 4 Winthrop Hall, Cambridge, Mass.  
 Panganiban, Elias H., College of Agriculture, University of the Philippines, Los Banos, P. I.  
 Patrick, Joseph C., Frigorifico Armour de La Plata, Calle Reconquista 314, Buenos Aires, Argentina, S. America.  
 Pendergast, Edward Hatton, 48 Bicknell St., Dorchester, Mass.  
 Postma, S., 53 Deventerweg, Zutphen, Holland.  
 Pritchard, Walter S., 1222 Rozelle Ave., Cleveland, Ohio.  
 Reese, J. Donald, 233 N. Pearl St., Crestline, Ohio.  
 Richardson, H. E., Mechanicsville, N. Y.  
 Robinson, Jesse, 7 Wave St., Cambridge, Mass.  
 Rosenfield, Harry, 132 Ziegler St., Roxbury, Mass.  
 Rumley, G. G., Roxana Petroleum Corp., Wood River, Ill.  
 Rutember, Charles B., 339 Seminary Ave., Carlinville, Ill.  
 Saenger, George W., Maize Products Pty., Ltd., Melbourne, Australia.  
 Schlundt, H. F., Chuquicamata, Chile, Chile Exploration Co., via Autopagasta, S. America.  
 Silverman, Louis, 1118 N. Euclid Ave., Pittsburgh, Pa.  
 Small, Lyndon F., 208 Warren St., Needham, Mass.  
 Spencer, Ernest F., Russia Cement Co., Gloucester, Mass.  
 Stevenson, Henry Arthur, Demerara Bauxite Co., Ltd., Akyma, British Guiana.  
 Stewart, Gertrude M., 2720 Salena St., St. Louis, Mo.  
 Stock, H. J., 12 Springhurst Ave., Toronto, Canada.  
 Sullivan, Willard Edmond, Lux Ave. & Pine Terrace, South San Francisco, Cal.  
 Suttle, Henry M., Viroqua, Wis.  
 Taylor, F. N. 1024 Ramona St., Corona, Cal.  
 Tooby, John J., 1000 Charles River Road, Cambridge 38, Mass.  
 Ulick, Joseph Carlyle, 4934 N. 9th St., Logan, Philadelphia, Pa.  
 Valin, Aime, 2 Place Youville, Montreal, Canada.  
 Vondrasek, Henry W., 3300 E. 55th St., Cleveland, Ohio.  
 Walker, Arthur J., Chem. Lab., Swift & Co., So. St. Joseph, Mo.  
 Walters, B. Frank, 19 E. 6th St., St. Paul, Minn.  
 Waser, R., Roxana Petroleum Corp., Refinery, Wood River, Ill.  
 Watkins, Charles F., Jr., 209 Chestnut St., New Bedford, Mass.  
 Weinberg, S., Chem. Div., U. S. Wool Co., 3562 N. Salmon St., Philadelphia, Pa.  
 Weir, J. W., Fillmore, Cal.  
 Yocum, Frank H., 168 Coit St., Irvington, N. J.  
 Young, Albert M., 8 Village St., Cambridge, Mass.
- CORPORATION MEMBERS.
- Alberent Stone Co., 223 E. 23rd St., New York City.  
 American Woolen Co., 245 State St., Boston, Mass.  
 Berger & Sons, Ltd., Lewis, Homerton, London, E.9, England.  
 The Borden Company, 108 Hudson St., New York City.  
 Church & Dwight Company, 27 Cedar St., New York City.  
 Cotton Research Co., Inc., 1020 Washington St., Boston, Mass.  
 Crane Co., 836 S. Michigan Ave., Chicago, Ill.  
 Duriron Co., Inc., The, Dayton, Ohio.  
 Goodrich Company, The B. F., Akron, Ohio.  
 Houghton & Co., E. F., Attention G. W. Pressel, 240 W. Somerset St., Philadelphia, Pa.  
 Pacific Coast Borax Company, 100 William St., New York City.  
 Pfizer & Co., Inc., Chas., 81 Maiden Lane, New York City.  
 Westinghouse Lamp Company, Bloomfield, N. J.

## MEETINGS OF SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

### CHICAGO SECTION.

On May 20, at the regular monthly meeting of the Section, Julius Stieglitz, of the Department of Chemistry, the University of Chicago, and Ex-President of the

American Chemical Society, gave a lecture on "The Electrical Theory of Oxidation." Attendance 34%.

The Annual Willard Gibbs Dinner and Award of Medal for 1921 to Mme. Marie Sklodowska Curie of the Curie Institute, College de France, occurred on June 14. The presentation address was by Julius Stieglitz, of the University of Chicago, and a review of Mme. Curie's work was made by H. N. McCoy.

S. I. REDMAN, *Secretary*.

#### CINCINNATI SECTION.

The 243rd regular meeting of the Section was held on May 18, when H. S. Fry spoke on "Electronic Tautomerism of Benzene Derivatives."

C. H. LUND, *Secretary*.

#### COLORADO SECTION.

The following officers for the Colorado Section have been elected: John B. Ekeley, chairman; R. S. Hiltner, vice chairman; C. W. Botkin, treasurer; Ruth B. Vertrees, secretary; W. D. Engle and S. J. Osborn, councilors.

RUTH B. VERTREES, *Secretary*.

#### DELAWARE SECTION.

At the regular meeting of the Section, held on May 2, Raymond F. Bacon, Director of the Mellon Institute, Pittsburgh, Pa., spoke on "The Technology of the American Sulfur Industry." After the lecture two moving pictures of "The Story of Sulfur" were shown.

On May 25, Edgar F. Smith, President of the American Chemical Society, addressed the members of the Section on "A Glance at the Early Organic Chemistry in the United States."

E. C. LATHROP, *Secretary*.

#### INDIANA SECTION.

The annual banquet of the Section was held on June 17, followed by a program for the entertainment of the members and guests.

EDGAR B. CARTER, *Secretary*.

#### IOWA SECTION.

On May 6, E. C. Franklin, Professor of Organic Chemistry in Leland Stanford Jr. University, addressed the Section on "Ammonium Compounds." The lecture was accompanied by actual demonstration work.

LEE E. CLARE, *Secretary*.

#### LEXINGTON SECTION.

The 71st meeting of the Section was held on May 26. The members made a visit to the plants of the Kentucky Steel Products Company and the Great Southern Refinery Company.

S. D. AVERITT, *Secretary*.

#### LOUISIANA SECTION.

On Friday, May 20, Carl F. Speh addressed the Section on "The Naval Stores Industry: Its Products and Their Industrial Importance."

H. R. STEVENS, *Secretary*.

#### MARYLAND SECTION.

The 51st meeting of the Section was held on May 27, when Ira B. Remsen addressed the members on "Personal Reminiscences of Sir William Ramsay." John W. Harrington, of the American Chemical Society News Service, spoke on the publicity work of the Society.

C. CLIFTON HOWES, *Secretary*.

## MINNESOTA SECTION.

L. S. Palmer, of the Department of Agricultural Biochemistry, University of Minnesota, addressed the Section on June 2, his subject being "Some Problems in Dairy Chemistry."

L. M. HENDERSON, *Secretary*.

## NEW YORK SECTION.

At the regular monthly meeting of the Section, held on June 10, the following program was given: "Committee on Industrial Alcohol of the American Chemical Society," by Martin H. Ittner; "Industrial Alcohol and Its Relation to Prohibition Enforcement from the Manufacturers' Standpoint," by M. C. Whitaker; "Industrial Alcohol and Its Relation to the Pharmaceutical and Perfumery Industries," by W. L. Crounse; "Industrial Alcohol and Its Relation to the Flavoring Extract and Food Industries," by F. M. Boyles; "Legal Status of Industrial Alcohol and Its Relation to Prohibition Enforcement," by Alfred D. Van Buren. Attendance, 23%.

H. G. SIDEBOTTOM, *Secretary*.

## NORTHEASTERN SECTION.

The regular monthly meeting of the Section occurred on June 10, at the Engineers Club in Boston, when the following program was rendered: "The Microstructure of Wood," by Allen Abram; "The Automotive Fuel Problem," by D. P. Barnard; "The Decolorization of Mineral Oils," by Leon W. Parsons; and "The Role of Compounding Ingredients in Rubber," by C. S. Venable.

L. F. HAMILTON, *Secretary*.

## PHILADELPHIA SECTION.

On May 19, the Section had as its speaker Treat B. Johnson, of Yale University, who took as his subject, "The Study of Organic Reactions Occurring in Living Matter." The after-dinner address was by George K. Helbert on "Concerning Patents."

J. HOWARD GRAHAM, *Secretary*.

## PUGET SOUND SECTION.

A joint meeting between the Local Section of the American Chemical Society and the Students' Section of the University of Washington was held on May 25. Oliver C. Ralston, of the U. S. Bureau of Mines, Seattle Experiment Station, spoke on "The Chemical Phases of the Hydrometallurgy of Zinc," and M. J. Falkenburg, of Seattle, made a report on the general meeting of the Society at Rochester.

R. W. ELLISON, *Secretary*.

## RHODE ISLAND SECTION.

On May 27, W. M. Saunders gave an illustrated talk on the "Lake Superior Iron District."

HERBERT F. DAVISON, *Secretary*.

## ROCHESTER SECTION.

The last meeting of the year, held on May 16, was addressed by the following: John Hudgings, of the Taylor Instrument Company, on "Chemical Thermometers," and R. F. Anderson, of the New York State Agricultural Experiment Station, on "Organic Phosphorus Compounds of Plants."

ERLE M. BILLINGS, *Secretary*.

## SAINT LOUIS SECTION.

On June 6, the following program was rendered before the Section: "Notes on Topping Petroleum," by F. W. L. Tydeman, of the Roxana Petroleum Corporation; and "Corrosion Prevention when Topping Petroleum," by R. R. Matthews, of the Roxana Petroleum Corporation.

H. A. CARLTON, *Secretary*.

## SAVANNAH SECTION.

The seventh regular meeting of the Section was held on May 26. The program consisted of a talk on "Scallops" by J. O. Clarke, and an address on "Some Phases of the Crude Drug Trade," by John J. McManus. Attendance, 50%.

HERBERT P. STRACK, *Secretary*.

## SOUTH JERSEY SECTION.

The eighth regular meeting of the Section was held on April 22. W. Lee Lewis, of Northwestern University, spoke on "Some Aspects of the Chemistry of Bacteria."

C. E. BURKE, *Secretary*.

## SOUTHERN CALIFORNIA SECTION.

At the regular monthly meeting of the Section, on May 26, a paper, entitled "The Lewis-Langmuir Hypothesis of Atomic Structure," by Howard J. Lucas, of the California Institute of Technology, was given.

H. I. PAYNE, *Secretary*.

## TOLEDO SECTION.

On May 13, Harry N. Holmes, Professor of Chemistry at Oberlin College, addressed the Section on the subject, "Emulsions."

The 37th regular meeting of the Section was held on June 3, when A. L. Grainger spoke on "Modern Pottery."

T. E. MOORE, *Secretary*.

## UNIVERSITY OF ILLINOIS SECTION.

The 115th regular meeting of the Section was held on April 20. R. E. Rindfusz, of the American Writing Paper Co., spoke on "The Manufacture of Paper."

S. A. BRALEY, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

On May 3, W. L. Badger addressed the Local Section on the subject of "The Boiling Points of Salt Solutions. Theoretical and Practical Considerations."

On June 7, F. W. Sullivan, Jr., addressed the Section, taking as his subject, "Diphenyl-beta-naphthyl-methyl."

C. C. MELOCHE, *Secretary*.

## UNIVERSITY OF MISSOURI.

The 100th meeting of the Section was held on May 12. A. G. Hogan read a paper on "The Influence of the Plane of Nutrition on the Maintenance Requirement of Cattle." Attendance, 69%.

H. D. HOOKER, Jr., *Secretary*.

## VIRGINIA SECTION.

The 43rd meeting of the Section was held on May 20. B. K. Steadman read a paper on "The Art of Paper Making."

At the last meeting of the Section the following officers for the year were elected: W. C. Jones, chairman; Graham Edgar, vice-chairman; Robert F. McCrackan, secretary-treasurer; W. F. Rudd and Garnet Ryland, councilors.

Robert F. McCRACKAN, *Secretary*.

## WASHINGTON, D. C. SECTION.

The 319th meeting of the Section occurred on May 12. The following program was given: "Quantitative Spectrum Analysis" (Illustrated), by W. F. Meggers, of the Bureau of Standards; "Estimation of Colorless Substances by Spectro-Photometric Methods," by W. E. Mathewson, Bureau of Chemistry; "A Direct Reading Spectro-

## WASHINGTON, D. C. SECTION.

Photometer for Measuring the Transmissivity of Liquids," by I. G. Priest, Bureau of Standards; "Polarimetry," by Frederick J. Bates, Bureau of Standards, and "Crystal Optics in Chemistry" (Illustrated), by F. E. Wright, Geophysical Laboratory.

The 320th meeting of the Section was held on May 25. Moving picture reels on the following subjects were shown: "The Story of Oil," "The Story of Armco Ingot Iron," and "The Story of Sulfur."

J. B. REED, *Secretary*.

## WESTERN NEW YORK SECTION.

At the annual meeting of the Section, held on May 10, the following officers were elected: R. C. Snowdon, Chairman; E. K. Strachan and H. N. Gilbert, Vice-Chairman; W. J. Marsh, Secretary; R. A. Nelson, Treasurer; D. H. Childs, R. H. Power and A. Schwarzman, Executive Committee; Walter Wallace, W. H. Watkins, C. G. Derick and A. M. Williamson, Councilors.

W. J. MARSH, *Secretary*.

## WISCONSIN SECTION.

The April meeting of the Section was held on April 20. Edward Kremers addressed the members on the subject, "Twenty-five Years of Chemical Research on a Typically American Genus of Plants."

At the regular monthly meeting of the Section, held on May 18, C. F. Burgess spoke on "The Chemist and the Business Man."

V. L. BOHNSON, *Secretary*.

## DECEASED.

Cohen, Mortimer J., 132 W. 113th St., New York City. Died April 2, 1920.

Gallup, F. L., Chemical Dept., E. I. du Pont de Nemours & Co., Wilmington, Del., Died in year 1920.

Hanley, Marguerite J., 118 W. 14th St., Minneapolis, Minn. Died April 30, 1921.

Lipstate, W. A., Box No. 600, Hastings-on-Hudson, N. Y. Died May 20, 1921.



# Proceedings.

## COUNCIL.

MEMBERS ELECTED BETWEEN JUNE 15 AND JULY 15, 1921.

Alexander, George Lehner, 306 Jackson St., Atchison, Kans.  
Allen, Woodward, 89 State St., Room 72, Boston, Mass.  
Brown, A. B. 211 Frick Building, Pittsburgh, Pa.  
Cooper, Philip, Amite, La.  
Csouka, F. A., 519 N. Highland Ave., Pittsburgh, Pa.  
Daley, Edward S., 5035 Fulton St., Chicago, Ill.  
Decotils, Horace, 116 Beacon Ave., Jersey City, N. J.  
Docter, Myron G., 680 Farwell Ave., Milwaukee, Wis.  
Gaylord, H. M., 25 Broadway, New York City.  
Grant, Albert Weston, Jr., Minnesota By-Product Coke Co., St. Paul, Minn.  
Hansen, Bjarne, Notodden Salpeterfabriken, Notodden, Norway.  
Heon, A. A., 923 Central Ave., Milwaukee, Wis.  
Herried, Myron T., 425 W. Dayton St., Madison, Wis.  
Hill, Albert, 3716 Revere Ct., Cleveland, Ohio.  
Hovland, Clifton R., Zumbrota, Minn.  
Kagesa, Setsuro, Students' Dormitory, Kyoto Imperial University, Kyoto, Japan.  
Klitsche, Charles H., American Blue Print Paper Co., 445 Plymouth Court, Chicago, Ill.  
Lieber, Alexander Dawson, 1117 N. Dearborn St., Chicago, Ill.  
Lewis, Bernard, 26 Lorne St., Dorchester, Mass.  
Lord, Erskine D., 3 Ivy St., Boston, Mass.  
McBurney, John D., 831 Gomer Ave., Cambridge, Ohio.  
Meredith, Henry, 106 Dumaresq St., Hamilton, N. S. W., Australia.  
Meyers, Harry M., 134 Fuller St., Brookline, Mass.  
Neef, Albert, Brusselsdestraat 87a, Maasricht, Netherlands.  
Payne, V. F., Palmer College, Albany, Mo.  
Phillips, E. Malcolm, 37 Hart St., Providence, R. I.  
Pitts, P. R., Acme Evans Co., Indianapolis, Ind.  
Redding, George K., 90 North St., North Weymouth, Mass.  
Rhodes, Irving C., 814 South Hope St., Los Angeles, Cal.  
Shidei, Jitaro, Chemical Institute, College of Science, Imperial University, Kyoto, Japan.  
Sirisook, S., 40 St. Stephen St., Boston, Mass.  
Skinner, Dwight S., 1229 Downing St., Denver, Col.  
Sulzner, C. F., Hotel Willard, 76th & West End Ave., New York City.  
Vogel, Frederick W., 1237 Narragansett Blvd., Providence, R. I.  
Young, A. A., 719 Pine St., Marquette, Mich.

## MEETINGS OF THE SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles F. Parsons, 1709 G St., N. W., Washington, D. C.)

### ARKANSAS SECTION.

The Arkansas Section of the American Chemical Society was organized on June 13, at the University of Arkansas, Fayetteville, Arkansas, the headquarters of the Section. The welcome address was given by Dean W. N. Gladson, Vice-President of the University. The Fayetteville Chamber of Commerce entertained with a complimentary dinner at the Hotel Washington. The following officers were elected: Charles F. Robinson, president; J. W. Johnson, vice-president; G. W. Roark, treasurer; J. W. Read, secretary; and Harrison Hale, counselor.

J. W. READ, *Secretary*.

### COLORADO SECTION.

At the regular monthly meeting of the Section, held on June 27, M. F. Coolbaugh spoke on "Some Anode and Cathode Reactions."

RUTH B. VETTERSS, *Secretary*.

## MIDLAND SECTION.

On June 1, J. A. Gann addressed the members of the Section, his subject being "Magnesium Piston Alloys." The new officers of the Section are: E. O. Barstow, chairman; M. E. Putnam, vice-chairman; J. A. Gann, secretary-treasurer; W. J. Hale, councilor; Thomas Griswold, Jr., I. A. Harlow, and C. W. Blenkhorn, executive committee.

J. A. GANN, *Secretary*.

## PHILADELPHIA SECTION.

A special meeting was held at the City Club on June 16, the topic for discussion being "Industrial Alcohol and Prohibition Enforcement." The following members of the American Chemical Society addressed the meeting; Martin H. Ittner, E. C. Lathrop, Chas. H. LaWall, A. A. Holmes, W. L. Crounse, George D. Rosengarten, Henry P. Busch.

J. HOWARD GRAHAM, *Secretary*.

## PITTSBURGH SECTION.

The annual outing of the Section was held on June 25. An elaborate program was carried out for the entertainment of the members and guests at "The Pines," near Pittsburgh.

G. STEGEMAN, *Secretary*.

## RHODE ISLAND SECTION.

The annual outing of the Section was held at the Rhode Island State College, Kingston, R. I. B. L. Hartwell, of the Rhode Island Experiment Station, gave a talk on "The Chemistry of Crop Experiments."

HERBERT F. DAVISON, *Secretary*.

## SYRACUSE SECTION.

The 150th regular meeting of the Section was held on May 27. L. E. Wise, of the New York State College of Forestry, spoke on "The Chemical Utilization of Wood."

K. B. NORTON, *Secretary*.

## TOLEDO SECTION.

At the June Meeting of the Section, the following officers were elected for the ensuing year: E. Schragenheim, chairman; Isadore L. Klein, vice-chairman; T. E. Moore, secretary-treasurer; W. B. Holmes, councilor.

T. E. MOORE, *Secretary*.

## DECEASED.

Ducas, B. P., 11 William St., New York City, died June 24, 1921.

Henderson, Ernest G., The Canadian Salt Co., Ltd., Windsor, Ont., Canada, died October, 1920.

Humbert, Ernest, Gresles, Seine Voise, France, died August, 1920.

Jackson, Kendrick C., 1751 Woodland Ave., N., Birmingham, Ala., died May 2, 1921.

Rose, L. H., Colonial Hotel, Chicago, Ill., died May, 1921.

# Proceedings.

## COUNCIL.

MEMBERS ELECTED BETWEEN JULY 15, AND AUGUST 15, 1921.

Abrams, J. H., 1519 N. Franklin St., Philadelphia, Pa.  
Asayeda, Nobutaro Onoda Cement Co., Shokou near Heijo, Korea, Japan.  
Baker, E. Meade, 206 Jackson St., Grove City, Pa.  
Barnes, Kenneth Boyd, 504 North First St., Rockford, Ill.  
Brown, Charles, 664 Walker Ave., Woodhaven, N. Y.  
Carleton, Phillips A., P. O. Box 13, New Westminster B. C. Canada.  
Cordero, Miguel, la Guerrero M. C. Hda de Su. Pedro, Coyoacan, Mexico.  
Cox, Irwin W., 1420 N. Ohio St., Lawrence, Kans.  
Daffin, John Baker, Arkansas College, Batesville, Ark.  
Deegan, Charles J., 217 W. Huron St., Chicago, Ill.  
Dougherty, D. J., 7701 Goodman Ave., Cleveland, Ohio.  
Farren, John W., P. O. Box 64, Grove City, Pa.  
Finn, George E., 10210 Kinsman Road, Cleveland, Ohio.  
Finney, Robert Spencer, 142 West 80th St., New York City.  
Hamby, T. P., Box 32, Athens, Tenn.  
Humphrey, Elizabeth, Montgomery, W. Va.  
Joss, Ernest J., Haskell, Okla.  
Kroh, James H., 1129 Lowry St., Duquesne, Pa.  
Kutscher, Charles F., P. O. Box 25, Grove City, Pa.  
Marsden, C. P., Jr., Red Tiles, Library Road, Library, Pa.  
Montgomery, Henry S., Celite Products Co., Lompoc, Cal.  
Mullin, J. A., 9619 Ramona Blve., Cleveland, Ohio.  
Oehlschlaeger, A. N., 2643 E. 122nd St., Cleveland, Ohio.  
Pierce, James Lewis, Marianna, Fla.  
Powell, Harry W., Dominion Cannery Lab., Brighton, Ont., Canada.  
Primley, Walter S., 133 W. Washington St., Chicago, Ill.  
Roth, Walter, Fernsprecher nr 111, Cothen, Anh. Germany.  
Snowden, Rene Revenel, 231 Douglas Bldg., Los Angeles, Cal.  
Thompson, John F., International Nickel Co., 67 Wall St., New York City.  
Vigneron, Henri, Societe Commerciale des Potasses d Olson, 25 West 43rd St., New York City.  
Winestock, Otto C., Perkinsville, Vermont.  
Zoeber, W. J., 1384 5th St., Oakland, Cal.

### CORPORATE MEMBERS.

Tinctura Laboratories, Inc., 85 Fort Greene Place, Brooklyn, N. Y.

## MEETINGS OF SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons,  
1709 G St., N. W., Washington, D. C.)

### CALIFORNIA SECTION.

The 24th Special Meeting of the California Section was in conjunction with the annual meeting of the Pacific Division of the American Association for the Advancement of Science, University of California, Berkeley, Cal., on August 5, 1921. The following program was given:

"Crystal Cleavage in Relation to Crystal Structure," by Dr. Arthur A. Noyes, California Institute of Technology.

"The Crum-Brown Substitution Rule and the Structure of Benzene," by Dr. Julius Stieglitz, University of Chicago, Acting Professor of Chemistry, Stanford University.

"Elementary Electrode Potentials," by Dr. Gilbert N. Lewis, University of California.

"Falsification in Early Chemical History," by Dr. J. M. Stillman, Stanford University.

"Ammono and Mixed Aqua Ammono Carbonic Acid," by Dr. E. C. Franklin, Stanford University.

"Studies in Protein Chemistry," by Dr. Carl Alsberg, Stanford University.

"The Crystal Structure of Potassium Cyanide," by Mr. Milton Bozarth, California Institute of Technology.

"Crystallographic Evidence in Regard to the Structure of Benzene," by Maurice L. Huggins, University of California.

LLOYD W. CHAPMAN, *Secretary-Treasurer*.

#### DECEASED.

Earnest J. Lederle, 453 Green Ave., Brooklyn, N. Y. Died July 21, 1921.

### NOTICE TO CANDIDATES INTENDING TO APPLY FOR A GRANT FROM THE "VAN'T HOFF FUND" FOR THE AID OF INVESTIGATORS IN THE FIELD OF PURE AND APPLIED CHEMISTRY.

According to the regulations of the "Van't Hoff-fund" founded June 28th, 1913, persons interested are notified that the foundation located in Amsterdam under the supervision of the Royal Academy of Sciences appropriates, from the income of the fund, annually, before March 1st, allotments to investigators in the field of pure and applied chemistry, who shall have applied for such a grant to the Committee charged with considering the applications and awarding the funds allotted.

At present this Committee is constituted as follows: A. F. Holleman, President; S. Hoogewerff, A. Smits, J. P. Wibaut, Secretary. If desirable the Committee may appoint still other members for one year only, to coöperate in judging the applications.

The names of persons to whom a grant is allowed, will be published. The grantees are requested to send to the Committee copies of papers giving the results of their work; but otherwise they are at liberty to choose the manner of publication, as well as the journal, in which to publish their results, only mentioning the fact, that the research was made with an appropriation from the "Van't Hoff-fund."

The amount available for 1922 is about fifteen hundred Dutch florins. Applications should be mailed registered to: Het bestuur der Koninklyke Akademie van Wetenschappen; bestemd voor de Commissie van het "Van't Hoff-fonds," Trippenhuys, Kloveniersburgwal, te Amsterdam, with a detailed account of the proposed use of the grant, the amount required, and the reasons upon which the candidates ground their claim. They must be received before November 1st, 1921.

In the name of the Committee of the "Van't Hoff-fund,"

A. F. HOLLEMAN, *President*,  
J. P. WIBAUT, *Secretary*.

Amsterdam, the month of July, 1921.

# Proceedings.

## GENERAL MEETING MINUTES.

The 62nd General Meeting of the American Chemical Society was called to order at Columbia University, New York City on Wednesday morning, September 7, 1921, with President Edgar F. Smith presiding. The welcoming address was delivered by Dr. John E. Teeple, Chairman of the New York Section, to which Dr. Smith responded in behalf of the Society.

The address of Hon. Francis P. Garvan on "Chemistry and the State" roused the audience to a high pitch of feeling regarding the present critical situation which chemistry in America is facing. The address of Sir William J. Pope on "Chemical Warfare" and of Professor R. F. Ruttan on "Organization of Industrial Research in Canada" were also received with enthusiasm. The addresses in full will appear in the October issue of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY.

Dr. Smith read the following telegram of greeting from President Harding, which had been originally received as the visiting guests crossed the border into the United States at Niagara Falls on Monday, September 5, 1921:

President Edgar F. Smith,  
American Chemical Society.

It is a pleasure to extend greetings to the gathering of American, Canadian and British Societies representing the chemical sciences and industries meeting on American soil. Probably none of the materialistic sciences holds promise of so great contributions to human welfare in the coming generations as that which your organization represents. The developments of applied chemistry involve both a possibility of vastly increased horrors in human conflict and alternately inestimable benefits to a peaceful civilization. Let us hope that a science so fraught with either good or vicious possibilities may be turned, through the wisdom of the nations, to the benefit and advancement of mankind.

WARREN G. HARDING.

The telegram was received with enthusiasm and the Society requested President Smith to express its appreciation in a suitable reply.

In accordance with the nominations of the Council, Sir William Pope and M. Paul Kestner were elected Honorary Members of the Society. Sir William responded in a delightful vein and expressed the extreme regret of M. Kestner at his inability to attend these meetings. Dr. Robert F. Ruttan, president-elect of the Society of Chemical Industry, and Dr. Ernst Cohen of the University of Utrecht were presented to the audience and heartily received.

The Committee appointed by the Council consisting of Messrs. H. T. Clarke, F. R. Eldred; and Chas. H. Herty submitted the following resolution, which was unanimously adopted:

Believing in the incalculable peace-time benefits which accrue from the development of the science of organic chemistry and its application in medicine, agriculture and the industries connected with foods, fuels, textiles and dyes;

Realizing the great rôle that organic chemistry has played in the development of chemical warfare, we call the attention of this nation to the grave crisis which threatens our organic chemical industry.

In spite of the tremendous strides made during the past five years in the United States, this important industry is still centered in Germany. Other nations have already sought to safeguard its future in their countries by appropriate legislation. America stands hesitant. Progress has been checked and indeed the very industry is threatened with destruction. Two agencies will be determinative in averting this disaster, the approaching International Conference on Disarmament and the Congress of the United States.

*Resolved, therefore,*

First, that we urge upon the American delegates to the Disarmament Conference most serious consideration of the broad question of chemical armament as affected by the development and maintenance of the chemical industries in the several nations.

Second, that we urge upon Congress the necessity of including in the permanent tariff bill a selective embargo for a limited period against importation of synthetic organic chemicals, and we express the confident hope that in view of the important bearing of such action on economical development and on national defense, our representatives regardless of political affiliations will support this legislation.

The fiftieth anniversary of Sir James and Lady Dewar's marriage having been recently celebrated, on August 8th, it was moved that a congratulatory message be transmitted from the American Chemical Society.

On Tuesday evening a complimentary smoker, with nearly one thousand members present, was held at the Waldorf-Astoria, and an interesting program consisting of music, vaudeville entertainment, cartoons, etc., was enjoyed by all.

At the International Meeting on Thursday afternoon, after an organ recital by Professor Samuel A. Baldwin in the grand hall of the College of the City of New York, which was greatly enjoyed by all, the following addresses were given:

**CHEMISTRY AND CIVILIZATION.**—Dr. Edgar F. Smith. Provost Emeritus, University of Pennsylvania, in the chair.

*Speakers.*

**SCIENCE AND CIVILIZATION: THE ROLE OF CHEMISTRY.**—Dr. Chas. Baskerville, Director of the Laboratories, College of the City of New York; Chairman, International Committee.

**ENERGY: ITS SOURCES AND FUTURE POSSIBILITIES.**—Dr. Arthur D. Little, Chemical Engineer and Technologist, Boston.

**THE ENGINEER: HUMAN AND SUPERIOR DIRECTION OF POWER.**—Dr. Leo H. Baekeland, Honorary Professor of Chemical Engineering, Columbia University.

**CHEMISTRY AND LIFE.**—Sir William J. Pope, Professor of Chemistry, Cambridge University.

**THEORIES.**—Dr. Willis R. Whitney, Head of Research Department, General Electric Company.

**RESEARCH APPLIED TO THE WORLD'S WORK.**—Dr. C. E. K. Mees, Head of Research Department, Eastman Kodak Company.

**PROBLEM OF DIFFUSION AND ITS BEARING ON CIVILIZATION.**—Professor Ernst Cohen, Professor of Chemistry, University of Utrecht.

**CATALYSIS: THE NEW ECONOMIC FACTOR.**—Prof. Wilder D. Bancroft, Professor of Physical Chemistry, Cornell University.

On Thursday evening the banquet hall at the Waldorf-Astoria was crowded at one of the Society's delightful gatherings, and on Friday night the members listened to the annual presidential address of Edgar F. Smith, entitled "Progress in Chemistry." This address was preceded by the unveiling of the Priestley Portrait, which is to be placed in the National Museum, the unveiling being accompanied by a description of the life and work of Priestley, by Dr. C. A. Browne.

The following Divisions and Sections met: Divisions of Agricultural and Food Chemistry, Biological Chemistry, Chemistry of Medicinal Products, Dye Chemistry, Fertilizer Chemistry, Industrial and Engineering Chemistry, Leather Chemistry, Organic Chemistry, Physical and Inorganic Chemistry, Rubber Chemistry, Sugar Chemistry, Water, Sewage and Sanitation Chemistry, and Sections of Cellulose Chemistry, Chemical Education, and Petroleum Chemistry.

At the meeting of the Division of Biological Chemistry a Committee was appointed, consisting of A. D. Emmett, Chairman, Alfred Hess, E. V. McCollum, L. B. Mendel, and H. C. Herman, to study and make recommendations regarding the standardization of methods for vitamine study.

Full details of the meetings of the Divisions will be found in the October issue of

the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY. The Divisions elected officers as follows:

- DIVISION OF AGRICULTURAL & FOOD CHEMISTRY: Chairman, T. J. Bryan; Secretary, C. S. Brinton.
- DIVISION OF BIOLOGICAL CHEMISTRY: Chairman, H. B. Lewis; Secretary, J. S. Hughes; Executive Committee, R. D. Swain, R. A. Dutcher, H. C. Sherman, H. F. Zoller, A. D. Emmett.
- DIVISION OF CHEMISTRY OF MEDICINAL PRODUCTS: Chairman, E. B. Carter, Secretary, E. H. Volwiler; Executive Committee, A. D. Hirschfelder, Charles E. Caspari.
- DIVISION OF DYE CHEMISTRY: Chairman, W. J. Hale; Vice-Chairman, L. A. Olney; Secretary-Treasurer, R. Norris Shreve; Executive Committee, B. A. Ludwig, R. E. Rose.
- DIVISION OF FERTILIZER CHEMISTRY: Chairman, F. B. Carpenter; Secretary, H. C. Moore.
- DIVISION OF INDUSTRIAL & ENGINEERING CHEMISTRY: Chairman, W. K. Lewis; Vice-Chairman, D. R. Sperry; Secretary, H. E. Howe; Asst. Secretary, E. M. Billings; Executive Committee, W. F. Hillebrand, Edward Mallinckrodt, Jr., F. M. DeBeers, Alexander Silverman, H. R. Moody, C. E. Coates.
- DIVISION OF LEATHER CHEMISTRY: Chairman, J. A. Wilson; Vice-Chairman, J. S. Rogers; Secretary, A. W. Thomas; Executive Committee, Frank L. Seymour-Jones, R. H. McKee.
- DIVISION OF ORGANIC CHEMISTRY: Chairman, H. T. Clarke; Vice-Chairman and Secretary, F. C. Whitmore.
- DIVISION OF PHYSICAL & INORGANIC CHEMISTRY: Chairman, S. E. Sheppard; Secretary, R. E. Wilson; Executive Committee, Wm. Blum, Joel Hillebrand, J. H. Mathews, L. C. Newell, H. B. Weiser, E. C. Bingham, G. S. Forbes.
- DIVISION OF RUBBER CHEMISTRY: Chairman, C. W. Bedford; Vice-Chairman, H. E. Simmons; Secretary, A. H. Smith; Executive Committee: W. B. Wiegand, W. W. Evans, J. B. Tuttle, D. F. Cranor, F. G. Breyer.
- DIVISION OF SUGAR CHEMISTRY: Chairman, S. J. Osborn; Vice-Chairman, F. W. Zerban; Secretary-Treasurer, F. J. Bates; Executive Committee: C. A. Browne, C. E. Coates, W. D. Horne, W. B. Newkirk, H. S. Paine, H. E. Zitkowski.
- DIVISION OF WATER, SEWAGE & SANITATION; Chairman, A. M. Buswell, Vice-Chairman, F. R. Georgia; Secretary-Treasurer, W. W. Skinner; Executive Committee, W. R. Copeland, W. D. Collins.

CHARLES L. PARSONS, *Secretary*.

## DIRECTORS' MINUTES.

The Directors met at the Chemists' Club, New York City, at 8 P.M., September 6th, with President Smith in the Chair, and Messrs. Bancroft, Bigelow, Little, Talbot, Teeple and Parsons present.

It was voted that the Treasurer be authorized to pay the unusual bills of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY due to the strike.

The Treasurer reported the following transactions in the funds of the Society, which were duly approved by the Directors:

The Treasurer will report the following transactions:

Bought

May 20	Columbus County, N. C.	\$10,066.44	Due 9/1	Temporary
May 27	City of Bristol	19,741.67	Due 7/20 and 9/15	Temporary

July 13	First 4 $\frac{1}{4}$ Liberty Bonds \$5,500 par value, reinvesting funds from Bonds which matured July 1	4,823.73		Morris Loeb
Aug. 22	City of Knoxville	19,870.00	Due 9/30	Temporary
Maturities				
May 10	Pan American Trading	\$7,500.00		Temporary
May 10	Birdsong Bros.	6,680.06		Temporary
July 1	5 Northern Pacific CB&Q	5,000.00		Morris Loeb
July 1	1 Northern Pacific CB&Q	1,000.00		General Inv.
July 20	City of Bristol	10,000.00		Temporary
Aug. 19	City of Spartanburg	10,300.00		Temporary
Sept. 1	City of Memphis	10,300.00		Temporary

It was voted to authorize the Treasurer to make loans and pledge the collateral of the Society therefor to an amount not to exceed \$40,000 when in his judgment it is necessary to do so to meet any excess of expenditures over receipts on 1921 account.

An appropriation of \$250.00 to Chemical Abstracts was made for the fitting up of an additional room.

It was voted that the Eschenbach Printing Company be given notice by the 1st of October, as required by the contract, that new bids on printing will be requested.

It was voted that the Secretary be authorized to sign a lease for the rooms now occupied by the Secretary's office for October 1921 to October 1922 on the basis of \$180.00 a month.

It was voted that the Editor of the *Journal of Industrial and Engineering Chemistry* be authorized to accept any proper advertisements, irrespective of their country or origin.

The Secretary presented requests from foreign libraries and individuals for complimentary copies of the Society's publications, the requests being necessary in the opinion of those making them on account of the present rate of exchange. It was voted that the Secretary insert an advertisement in the Society's journals bringing to the attention of members the need of the journals by certain universities and scientific laboratories, in order that they might make donations thereto if they see fit. It was the opinion of the Directors, however, that the Society itself, in view of the fact that it is at present facing a deficit, is not in position to make such donations.

The ad interim report of the Finance Committee, which was present, indicated that the actual expenditures for the year 1921 are apt to exceed the receipts by approximately \$10,000.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*.

### ADVISORY COMMITTEE MINUTES.

The Advisory Committee met at the Chemists' Club, New York City, on Tuesday, September 6th, at 12 o'clock, with President Smith in the Chair and Messrs. Howe, Nichols, Rosengarten, and Parsons present.

The Secretary was instructed to put no names of companies on the programs of meetings nor to include a paper as coming from any particular laboratory or having other than an individual, or individuals as authors.

An invitation was presented for the American Chemical Society to be represented at the inauguration of John Martin Thomas as President of the Pennsylvania State College, Friday, October 14th. Dr. Edgar F. Smith was designated as the delegate.

The Advisory Committee recommended to the Directors that the Editor of the



Journal of Industrial and Engineering Chemistry be authorized to accept all proper advertisements, irrespective of their country or origin.

The Advisory Committee directed the Secretary to present the names of Wm. M. Burton and Hugh K. Moore to the Secretary of the New York Section of the Society of Chemical Industry as their suggestion of recipients of the Perkin Medal.

CHARLES L. PARSONS, *Secretary*.

## COUNCIL MINUTES.

The Council of the American Chemical Society met in Rumford Hall, Chemists' Club, New York City, at 3 P.M., Tuesday, September 6, 1921, with President Edgar F. Smith in the chair, and the following Councilors present:

*Ex-Officio*.—W. D. Bancroft, W. D. Bigelow, F. B. Carpenter, E. J. Crane, A. B. Davis, A. W. Dox, C. H. Herty, H. N. Holmes, A. D. Little, W. H. Nichols, W. A. Noyes, C. L. Parsons, H. P. Talbot, J. E. Teeple.

*Councilors-at-Large*.—H. E. Howe, L. W. Jones, Wm. McPherson, A. Rogers, G. D. Rosen-garten.

*Local Sections*.—*Arkansas*, Harrison Hale. *California*, R. E. Swain. *Chicago*, T. J. Bryan, W. V. Evans (subs. for A. M. Taylor), D. K. French (subs. for R. J. Quinn), C. H. Jones (subs. for L. M. Tolman), H. N. McCoy, G. A. Menge (subs. for W. R. Smith), L. V. Redman, G. L. Wendt (subs. for C. S. Miner), F. C. Whitmore (subs. for W. D. Richardson). *Cincinnati*, H. M. Campbell (subs. for C. P. Long), M. B. Graff, A. P. Mathews. *Cleveland*, A. W. Smith. *Columbus*, M. Hollingsworth (subs. for W. E. Henderson), A. M. Patterson (subs. for G. O. Higley). *Connecticut Valley*, J. S. Chamberlain, C. R. Hoover. *Delaware*, G. M. Norman, C. L. Reese. *Detroit*, H. T. Graber (subs. for H. C. Hamilton). *Georgia*, C. E. Brett (subs. for T. C. Law). *Indiana*, F. R. Eldred. *Iowa*, Edward Bartow. *Kansas City*, F. B. Dains. *Lehigh Valley*, E. C. Bingham. *Louisiana*, C. E. Coates. *Maryland*, H. R. Gundlach, B. F. Lovelace. *Midland*, Wm. J. Hale. *Milwaukee*, E. J. Kern (subs. for G. N. Prentiss), J. A. Wilson. *Minnesota*, R. A. Gortner (subs. for E. P. Harding), C. A. Mann. *Nebraska*, F. W. Upson. *New Haven*, W. R. Hibbard. *New York*, Chas. Baskerville, C. A. Browne, C. E. Davis, F. E. Dodge, V. C. Edwards, Ellwood Hendrick, M. H. Ittner, D. W. Jayne, James Kendall, A. C. Langmuir, K. G. MacKenzie, L. J. Matos, R. H. McKee, F. J. Metzger, C. F. Roth, H. G. Sidebottom (subs. for David Wesson), G. C. Stone, G. W. Thompson, B. R. Tunison, L. van Doren (subs. for S. A. Tucker), R. G. Wright, J. E. Zanetti (subs. for D. D. Van Slyke). *North Carolina*, A. S. Wheeler. *Northeastern*, G. L. Coyle, W. C. Durfee, G. S. Forbes, W. L. Jennings, J. F. Norris, R. S. Weston, R. E. Wilson (subs. for W. K. Lewis). *Omaha*, Wm. M. Barr. *Philadelphia*, G. E. Barton, E. C. Bertolet, W. C. Carnell, J. S. Goldbaum, J. H. Graham (subs. for A. M. Comey), E. F. Hicks, H. S. Miner, W. T. Taggart. *Pittsburgh*, H. V. Churchill, A. C. Fieldner, Alex. Silverman, H. C. Weber (subs. for J. O. Handy), E. R. Weidlein (subs. for E. W. Tillotson). *Rochester*, H. T. Clarke, H. LeB. Gray. *Savannah*, H. S. Bailey (subs. for F. N. Smalley). *South Dakota*, B. A. Dunbar. *South Jersey*, H. D. Gibbs (subs. for Wm. Kirk). *St. Louis*, E. Mallinckrodt, Jr. *Syracuse*, R. A. Baker (subs. for A. C. Houghton). *Univ. of Illinois*, Roger Adams, *Univ. of Michigan*, A. H. White (subs. for H. H. Willard). *Washington*, Wm. Blum (subs. for F. C. Smithers), W. M. Clark, W. D. Collins, A. Seidell, R. B. Sosman. *Western New York*, C. G. Derick, A. M. Williamson. *Wisconsin*, Victor Lenher.

The following report of the Patent and Related Legislation Committee was pre-sented.

### REPORT

—OF THE—

### PATENT AND RELATED LEGISLATION COMMITTEE

—ON—

### STANLEY PATENT BILL, S. 1838.

A bill has been introduced in the United States Senate, which seeks to amend our patent law in a way that requires the gravest attention from all who are interested in our patent system.

This bill, Stanley Patent Bill, S. 1838, while seemingly harmless on its face, is believed by your Committee on Patent and Related Legislation to be, on the one hand, of little practical value to accomplish the purpose for which it is introduced, and, on the other hand, to involve possibilities of great harm to the patent system as a whole.

The bill was introduced at the request of the Secretary of War because inventions relating to ordnance, which had been made by American engineers and not patented by them, are being patented on applications for patent which have been sold to the Krupps, so that there is apparently danger of our not being able to use in our own defense inventions made by Americans. The Stanley bill seeks to prevent this situation by granting patents to aliens only on condition that the government shall

have the right to grant licenses under the patents, unless they are worked to an adequate extent in this country within two years from their issuance.

Your Committee wishes to state at the outset that the remedy for this situation lies in proving, when suit is brought under such a patent, that the invention was made and publicly used in this country and was not originated by the German patentee. Proof of these facts would result in the patent being held to be invalid. It is not necessary to introduce a compulsory working clause into our patent system as a defense against such a patent.

If the purpose of the law is also to discourage the Germans from taking out patents in the United States, that also would seem to be ineffective. For, if the invention is one of sufficient value, so that Americans would want licenses under the patent, it would be of enough value to make it worth while for the Germans to manufacture in this country to prevent the monopoly being weakened or destroyed by the granting of licenses under the patent. If the invention were of so little importance that it was not worth while for the Germans to work it in this country, then it would probably be of so little value that no one would want a licence under the patent.

If United States patents were only granted to Germans under such onerous terms that they were not worth while taking out, then where the invention were of such a nature that it could be practiced secretly, such as chemical inventions, the Germans would only manufacture in Germany and not patent it anywhere, and thus our public would be deprived of that knowledge of the invention which would be obtained from a patent, and by which they could practice the invention when the patent had expired.

To the extent to which the Bill would compel the Germans to manufacture in this country, it would tend to cause that "peaceful penetration" which was so objectionable before we went into the war and which we took so much trouble to root out during the war.

The infant dye industry in this country is seeking protection from German competition and is now protected by an embargo preventing the importation of German dyes which are adequately manufactured in this country. It is imperative that we have a well-equipped and extensive dye industry in this country. The German dye industry was the root and foundation of Germany's manufacture of explosives, poison gases, and means of protection from poison gases. It was because the chemistry of these munitions of war is intimately related to the chemistry of dyes and because the dye plants were readily converted to war uses that Germany was enabled to produce such enormous quantities of explosives, against which there was no immediate defense. The protection and encouragement of a dye industry and other chemical industries are therefore necessary measures for our defense. It would therefore seem highly unwise to put pressure on the Germans, through our patent laws, to manufacture in this country.

There is some belief among legislators and others that a compulsory working requirement, under penalty of having licenses granted, should be applied to all United States patents, whether granted to domestic or foreign inventors, and if the Stanley bill were enacted making such a requirement as to patents granted to foreign inventors, it would be an entering wedge by which there is danger that such a requirement would be applied to our patents generally. This your Committee believes would be disastrous to our patent system.

The prime object of our patent system was to induce the production of inventions. The reward held out as an inducement to invent was an exclusive monopoly of the invention for seventeen years, during which time the inventor might make money out of the invention if it had merit and he had business ability enough to supply it to the public.

The path of the inventor is already strewn with difficulties and a large proportion of inventors make little or nothing from their inventions, and if those which would otherwise be successful are handicapped much more than they are to-day, your Committee believes that the production of inventions will be greatly decreased.

Our patent system has been of inestimable value to our country and more than any other factor has helped to place our country in the position of the greatest inventive, manufacturing and agricultural country in the world. Therefore, changes in that system should only be made after the most mature consideration and a clear demonstration that those changes will either increase, or at least not impair, the production of inventions.

Among the harmful reactions of a compulsory working requirement are the following:

An invention which is admirable in itself may find no market for many years because the things or conditions with which it has to work have to grow up to the advance made by the invention. In such a case the expense of working the invention—and it would always be considerable—would be entirely lost, and usually the inventor would allow the patent to lapse for failure to work. If, as not infrequently happens, such an invention would find a good market during the later years of its life, which could not have been foreseen when the patent was issued, the patentee and other inventors seeing what he had lost by the compulsory working requirement would be embittered against the patent system and would cease to invent.

Most concerns which buy or manufacture under patents will not have anything to do with them unless they can have a complete monopoly. Where licenses have been granted under a patent for failure to commercially work the invention, the salability of the patent would usually be largely destroyed for this reason.

The making of an invention to-day is not usually the making of a single patent, but is the result of a long development through which a series of patents is taken out, and often auxiliary inventions are patented, such as machines, apparatus or processes for making the desired product. Thus, the inventor or manufacturer would have a group of patents whose dates of issue would be scattered along over a series of years. Although it would not be known until the end of the development had been reached whether the enterprise would ever justify going on the market, each of the series of patents would have to be worked under the Stanley Bill within two years after it was issued under penalty of having a competitor have a license under that patent, although the license might be demanded just for the purpose of making trouble with the enterprise. If this were the situation, even large corporations would often hesitate to face the expense involved in perfecting a patent and would refrain from development, to the loss of the public.

If the law were changed, as proposed in the Stanley Bill, the wealthy man could afford to obtain patents, while the poor man could not. It is one of the proud distinctions of our patent system that its doors are open equally to all men. Many a man in the United States has raised himself from the bench to the ownership of a business by his inventions. There are many businesses to-day which are founded upon the inventions of their principal owners, who made them when they were poor men.

If the compulsory working requirement had benefitted those countries in which it is a feature of their patent laws, there would be more reason for trying it in the United States, but there is no country which at all approaches the number of patents or valuable inventions per capita that are produced in the United States. Even the very small inventions which are brought into being by our patent system are often of great value to the public, although they may be of no value to their inventors, because they lead a development along step-by-step until it reaches a point from which some one sees an opportunity to make a really great advance in the art.

In 1832 the United States enacted a compulsory working clause, but in 1836 it was repealed, and no such clause has ever been re-enacted.

Your Committee believes that, as a practical matter, the Stanley Bill would only accomplish a comparatively small amount of good and on the other hand its possibilities for harm are so great that it would be exceedingly unwise to make it a law, and your Committee therefore respectfully advises that the American Chemical Society exercise its influence to prevent the enactment of the bill.

Respectfully submitted,

EDWIN J. PRINDLE,  
E. A. HILL,  
A. SCHMIDT,  
C. P. TOWNSEND,  
EDMOND O'NEIL.

After extended discussion it was felt that the report as it stood might give a wrong impression of the Society's feelings if presented unchanged to Congress. It was accordingly voted:

"While the Council is disposed to accept the views of its Committee on Patents, nevertheless it is felt that a constructive suggestion should be made by the Committee as to legislation which would prevent the utilization of our patent office by foreigners for the suppression of the development of industries, such as was so clearly apparent in the organic chemical industry upon our entrance into the war in 1917. The Committee is therefore urged to consider this problem immediately and to report to the Committee on National Policy."

The Council voted to form a Division of Sugar Chemistry. The following by-laws presented by the Sugar Section, being found to be in conformity with the constitution and by-laws of the Society, were adopted by the Council.

#### CONSTITUTION OF THE DIVISION OF SUGAR CHEMISTRY AND TECHNOLOGY OF THE AMERICAN CHEMICAL SOCIETY.

##### ARTICLE I.

##### *Name and Object.*

*Sec. 1.* The name of this organization shall be the Division of Sugar Chemistry and Technology of the American Chemical Society.

*Sec. 2.* The object of the Division shall be the stimulation of interest, the encouragement of research and the diffusion of information in all that pertains to the chemistry and technology of sugars.

*Sec. 3.* It is not the purpose of this organization to supplant other local organizations of American sugar chemists or technologists already existing or that may exist, but rather to coöperate with these associations for promoting the objects which they have in common.

## ARTICLE II.

*Membership.*

*Sec. 1.* There shall be two classes of members:—active and associate.

*Sec. 2.* Active membership shall be open only to members of the American Chemical Society. Any such member, who is interested in the object of the Division and who shall apply to the Secretary-Treasurer, can be enrolled as an Active Member.

*Sec. 3.* Any person who is interested in the object of the Division and who is not a member of the American Chemical Society may be enrolled as an Associate Member.

*Sec. 4.* Associate Members shall be entitled to all privileges of the Division, save that of voting for officers and of holding office; provided, that such associate members shall not be entitled to any of the other privileges of the American Chemical Society, and shall pay dues of two dollars (\$2.00) per annum, in addition to such other dues as the Division may require. Associate Members may become Active Members upon joining the American Chemical Society.

## ARTICLE III.

*Officers.*

*Sec. 1.* The officers of the Division shall be a Chairman, a Vice-chairman, a Secretary-Treasurer, and an Executive Committee.

*Sec. 2.* The Executive Committee shall consist of the Chairman, Vice-chairman, Secretary-Treasurer and six other active members of the Division.

*Sec. 3.* At the first session of the Division during the annual meeting of the American Chemical Society and following the report of the Secretary-Treasurer, the Chairman shall appoint from the members present at the meeting, a committee of three to nominate officers for the ensuing year. This committee shall present its list of nominations immediately before the election of officers at the last session of the Division during that annual meeting.

*Sec. 4.* All officers shall be elected by ballot of the Active Members present at the last session of the Division during the annual meeting of the American Chemical Society, and shall take office at the close of the meeting at which they were elected. They shall hold office for one year or until their successors are elected.

*Sec. 5.* Vacancies of office which may occur between meetings shall be filled by the Executive Committee.

*Sec. 6.* It shall be the duty of the Chairman to represent the Division in the Council of the American Chemical Society, to preside at the meetings of the Division and of its Executive Committee, and to execute the decisions and recommendations of this Committee.

*Sec. 7.* In the absence of the Chairman the duties of his office shall be filled by the Vice-Chairman.

*Sec. 8.* It shall be the duty of the Secretary-Treasurer to record and preserve the minutes and proceedings of the Division and of the Executive Committee, to keep a list of the Active and Associate members, to send members such notices as may be required and any available reprints of papers which are read at the meetings, to transmit to the Secretary of the American Chemical Society the names of all officers and committees of the Division within three weeks of their appointment and to notify the Secretary of the American Chemical Society of any changes in officers and committees during the year. The Secretary-Treasurer shall also have charge of the funds of the Division and shall make such disbursements therefrom as may be authorized by the Executive Committee.

*Sec. 9.* The Executive Committee shall manage the affairs of the Division and shall appoint, and direct the work of, the special committees. As early as possible at each general meeting of the Society the Executive Committee shall meet to consider the business of the Division and receive the reports of the special committees. The Executive Committee shall authorize the disbursements of funds to be made by the Secretary-Treasurer.

## ARTICLE IV.

*Sec. 1.* There shall be a meeting of the Division at each general meeting of the American Chemical Society. The order of business shall be as follows:

Reading of Minutes.

Report of Executive Committee.

Report of Secretary.

Appointment of Nominating Committee (first session of annual meeting).

Report of special committees and discussion.

Reading of papers and discussions.

Report of Nominating Committee (last session of annual meeting).

Election of officers (last session of annual meeting).

Miscellaneous business.

*Sec. 2.* Members of the Division who may desire to meet at other times than those of the two general meetings of the American Chemical Society have the privilege of participating in the monthly meetings of any of the local sections of the American Chemical Society.

#### ARTICLE V.

##### *Special Committees.*

*Sec. 1.* The Chairman, with the advice and approval of the Executive Committee, shall appoint such standing committees as may be necessary to consider, transact and report upon, special matters of business.

#### ARTICLE VI.

##### *Publications.*

*Sec. 1.* The official organs of the Division shall be the *Journal of the American Chemical Society* and the *Journal of Industrial and Engineering Chemistry*. Authors who intend to publish the papers which are read before the Division must submit their contributions to the editor of either of these journals before they can be published elsewhere.

*Sec. 2.* If the editors consider a paper too technical, or for any other reason, unsuited for publication in the Society's Journals, the author is then at liberty to publish it in such sugar trade or other periodicals as he may desire, with the statement, however, that the paper was read before the Division at a specified meeting of the American Chemical Society.

*Sec. 3.* Authors, who publish papers that are read before the Division, shall, in all cases, order for the Secretary-Treasurer a sufficient number of reprints, as uniform as possible in 6 inch x 9 inch size, to supply the active and associate members of the Division, any cost for such reprints to be paid by the Secretary-Treasurer from the funds of the Division.

*Sec. 4.* The Executive Committee may at its discretion and with the approval of the Council of the American Chemical Society, provide for the issue of other publications.

#### ARTICLE VII.

##### *Decision of Questions.*

*Sec. 1.* All questions concerned with organization, such as election of officers, rules of procedure, order of business, etc., shall be decided at the meetings of the Division by a vote of the Active Members, then and there present.

*Sec. 2.* All questions not concerned with organization, such as methods of analysis and general matters of policy, shall be decided only by letter ballot of all Active Members of the Division and such decisions to be effective must be approved by the Council of the American Chemical Society.

#### ARTICLE VIII.

##### *Assessments.*

*Sec. 1.* The Executive Committee may at its discretion impose dues not to exceed two dollars (\$2.00) per annum upon the Active and four dollars (\$4.00) per annum upon the Associate Members of the Division, such dues for Associate Members to be in addition to the membership dues required under Article II, Section 4. All dues shall be collected by the Secretary-Treasurer and the disbursements therefrom shall be devoted to the purpose of the Division.

#### ARTICLE IX.

##### *Amendments.*

*Sec. 1.* Amendments to this Constitution shall be made only at the Annual Meeting of the Division by a two-thirds majority of the Active Members present, provided that a two months notice of the proposed amendment with the text of the same has been sent to the Active Members of the Division.

*Sec. 2.* The amendments of the Constitution to be effective must be approved by the Council of the American Chemical Society.

It was voted to form a Division of Leather Chemistry. The following by-laws presented by the Leather Section, being found to be in conformity with the constitution and by-laws of the Society, were adopted by the Council.

#### BY-LAWS OF LEATHER DIVISION OF THE AMERICAN CHEMICAL SOCIETY.

##### ARTICLE 1.—NAME.

This Division shall be known as the LEATHER DIVISION of the American Chemical Society.

##### ARTICLE 2.—MEMBERSHIP.

Any member of the Society may become a member of the Division by filling out, signing, and sending to the Recording Secretary of the Division a form essentially the same as that given below

and shall remain a member so long as he fulfills the obligations imposed by the Division upon its members.

FORM OF APPLICATION FOR MEMBERSHIP: I, (*give name in full*), a member of the American Chemical Society, do hereby request the Recording Secretary of the Leather Division to enter my name as a member of the Division and I agree to observe the rules and by-laws of said Division so long as I remain a member.

#### ARTICLE 3.—OFFICERS AND MANNER OF ELECTION.

1. The officers of the Division shall be a Chairman, a Vice-chairman a Recording Secretary, and an Executive Committee consisting of the Chairman, Vice-chairman, Recording Secretary and two registered members of the Division.

2. The Chairman of the Division shall be Chairman of the Executive Committee.

3. The officers of the Division shall be nominated by a committee, appointed by the Chairman, and shall be elected annually by ballot at the last session of the Division, held during the annual meeting of the Society, and shall take office at the close of the meeting at which they were elected. They shall hold office until their successors are elected.

4. The Executive Committee shall fill any vacancies that may occur through death or resignation among officers of the Division.

#### ARTICLE 4.—DUTIES OF OFFICERS

1. It shall be the duty of the Chairman to represent the Division in the Council of the Society; to preside at meetings of the Executive Committee; to carry into effect the decisions and recommendations of that Committee; to preside at stated meetings of the Division; and to report to the Society at its regular meetings.

2. In the absence of the Chairman, the duties of his office shall devolve upon the Vice-chairman.

3. It shall be the duty of the Recording Secretary to keep a record of the proceedings of the Division and of the Executive Committee; to maintain a list of registered members; to send to registered members such notices as the business of the Division may require; and to transmit to the Secretary of the Society the names of all officers and standing committees of the Division within ten days of their appointment, and, in like manner, to notify the Secretary of the Society of any change of officers or standing committees during the year. The Recording Secretary shall be the custodian of the files of the Division; shall make all disbursements, subject to the authorization of the Executive Committee; and shall report to the Division at its annual meeting.

4. The Executive Committee shall conduct the business of the Division and direct its activities. As early as may be, the Committee shall, at each general meeting, hold a meeting to consider the affairs of the Division and receive reports of its committees. The voting majority of the Executive Committee shall be responsible for all expenditures which it may authorize, except so far as the action of the Council shall have previously provided for such expenditures.

#### ARTICLE 4.—MEETINGS.

1. There shall be a meeting of the Division at each annual meeting of the Society and, unless the Division by a two-thirds vote of the registered members present at the preceding annual meeting shall determine otherwise, also at each general meeting of the Society other than the annual meeting. Business affecting the organization of the Division shall be transacted only at the meeting coincident with the annual meeting of the Society.

2. The order of the business shall be as follows:

- a. Reading of minutes of previous meeting.
- b. Reports of the Chairman and Secretary.
- c. Report of the Executive Committee.
- d. Reports of committees and discussions.
- e. Reading of papers and discussions.
- f. Miscellaneous business.
- g. At the Annual Meeting—Election of Officers.
- h. Unfinished business.

The regular order of the business of the Division may be suspended at any session by the consent of two-thirds of the members of the Division present.

#### ARTICLE 6.—SPECIAL AND STANDING COMMITTEES.

The Chairman shall appoint from time to time committees of the Division to consider, conduct, and report upon special matters as may be delegated to them.

#### ARTICLE 7.—PUBLICATION.

The Executive Committee may, at its discretion, provide for the issue of publications for distribution to registered members of the Division, or for sale. The official organs of the Division are to be the *Journal of the American Chemical Society* and the *Journal of Industrial and Engineering Chemistry*.

No paper presented before the Division shall be published in any journal other than those of the Society, until after prior publication in one of the Society's journals, or until the consent of one of the editors of the Society's journals has been obtained.

#### ARTICLE 8.—ASSESSMENTS.

The Executive Committee may, at its discretion, impose dues not to exceed two dollars per year upon registered members of the Division, said dues to be collected by the Secretary, and the receipts therefrom to be devoted to the purpose of the Division. The Executive Committee may drop from the registered membership in the Division the name of any member who is in arrears for dues for over one year.

#### ARTICLE 9.—AMENDMENTS.

These by-laws may be amended at any annual meeting of the Division by a three-fifths vote of the registered members present, provided two weeks notice of the proposed amendment with text thereof has been sent to the registered members of the Division. The amendment to be effective must be approved by the Council and accepted by that body as not inconsistent with the Constitution and By-laws of the Society.

Ten members of the Society having proposed the names of Sir William J. Pope, K.B.E., F.R.S., and M. Paul Kestner for honorary membership in the American Chemical Society, their names were presented to the Council, and having been endorsed in writing by a majority of the Council, as required by the constitution, the Council instructed the Secretary to present their names to the General Meeting for action, with the recommendation of the Council that they be elected.

It was voted, in view of the fact that the South Carolina Section was apparently in a state of coma, not having held a meeting for several years, and the matter having been taken up with the officers of that Section by the Secretary, that the charter of the South Carolina Section be withdrawn.

It was voted to hold the Annual Meeting in September 1922 in Pittsburgh, Pa. It was voted to leave the date of the Spring Meeting to be held in Birmingham, Ala., to the President and the Secretary with power.

Arthur B. Lamb was reelected Editor of the *Journal of the American Chemical Society*. The term of office of Associate Editors G. P. Baxter and H. W. Wiley having been ended by lot, it was voted that their successors be named by Dr. Lamb, subject to the approval of the President.

Charles H. Herty was reelected Editor of the *Journal of Industrial and Engineering Chemistry*, with the following Advisory Board: H. E. Barnard, Chas. E. Coates, Ralph Gould, Wm. Hoskins, A. D. Little, Geo. D. Rosengarten, T. B. Wagner.

E. J. Crane was reelected Editor of *Chemical Abstracts*.

W. A. Noyes was reelected Editor of Scientific Monographs, with the same board of Associate Editors.

John Johnston was reelected Editor of Technological Monographs, and the selection of successors to the two retiring editors, C. L. Reese and C. P. Townsend, was left to Dr. Johnston and the President with power.

Dr. Smith spoke of the work of the Priestley Memorial Committee and of the Priestley portrait presented preceding President Smith's address on Friday evening, and outlined the plans of the Committee to establish a Priestley Medal fund with the remaining funds. President Smith described the plans for the reestablishment of the Priestley home at Northumberland, Pa., and spoke feelingly of his wish that the Society might be able to celebrate its fiftieth anniversary with a meeting at Northumberland in 1925.

The ad interim report of the Finance Committee sent to the members of the Council was brought before the Council for discussion.

The Committee on a proposed amendment to Article 13 of the constitution reported as follows:

The committee have carefully considered the amendment in question and have

consulted the records with reference to requests made by Sections at the present time, as well as the financial condition of the Society. In view of the present conditions the committee recommend that the amendment be not adopted.

H. LEB. GRAY,  
A. V. H. MORY,  
H. E. HOWE.

It was moved that the whole latter be laid on the table until the Annual Meeting in September 1922.

After an extended discussion, the following resolutions were unanimously passed:

WHEREAS, the American Chemical Society has provided through its News Service ample means for reaching the public promptly and uniformly,

Therefore, be it *resolved*:

That officers of all Divisions and Sections are instructed to file with the Secretary of the Society all matter for which they desire publicity, including abstracts, and that this material be supplied only to the News Service through the General Secretary's office.

Whereupon the Director of the News Service presented a report on the method adopted by the News Service for the New York Meeting for the distribution of abstracts and asked for discussion. It was felt that this method would relieve the individual secretaries of the divisions from a great deal of routine work, at the same time establishing a thoroughly coördinated service.

John E. Teeple, President of the Chemists' Club, presented a suggestion that the Society take over the Bureau of Employment now run by the Chemists' Club in New York City or establish a bureau of its own to replace this organization. It was voted that a committee of three be appointed by the President to consider plans and possibilities and report at the Spring Meeting. The President appointed Wm. McPherson, Chairman, Edward Bartow, and A. C. Fieldner.

The Secretary read a letter from the Committee on Publications outlining the progress made since the strike in the printer's plant on May 1, indicating that publications will be on a normal basis by October 1.

Dr. Smith spoke regarding the present legislative situation with regard to the organic chemical industry, whereupon it was moved that a committee be appointed to draft resolutions urging the passage of a limited embargo on synthetic organic chemicals and present them at the General Meeting of the Society. President Smith appointed H. F. Clarke, Chas. H. Herty, and Frank R. Eldred.

The Council directed the Secretary to express its unanimous and hearty thanks to the New York Section, to the members of the various committees, to Columbia University, to the Chemists' Club, to the College of the City of New York, and to others who had extended hospitality to the Society.

The meeting adjourned at 5.10 P.M. At 6.30 the Councilors met in the dining hall of the Chemists' Club for dinner, as guests of the Local Section.

CHARLES L. PARSONS, *Secretary*.

#### MEMBERS ELECTED BETWEEN AUGUST 15 AND SEPTEMBER 15, 1921.

Baizer, Roland W., 636 East 18th St., Brooklyn, N. Y.  
Baril, Georges, Université de Montreal, 185 rue St. Denis, Montreal, Canada.  
Bartlett, W. J., 1721 Coit Ave., East Cleveland, Ohio.  
Bradshaw, Lawrence, 50 East 41st St., New York City.  
Brau, Bozotech C., Vanity Fair Silk Mills, Reading, Pa.  
Brook, George Bernard, British Aluminium Co., Kenochleven, Argyll, Scotland.  
Brown, William, Eastern Smelting Co., Ltd., Daloh Kramat Road, Penang, S. S. Hongkong, China.  
Burton, Georgia W., Greenville Woman's College, Greenville, S. Car.  
Caius, J. F., St. Joseph's College, Trichinopoly, South India.



Caldwell, Mary L., 620 West 116th St., New York City.  
 Caswell, Anne T., Milwaukee-Downer College, Milwaukee, Wis.  
 Catlett, Geo. F. State Board of Health, Raleigh, N. Car.  
 Chen, Kwan-Shun, 104 Harvard Place, Ithaca, N. Y.  
 Cook, Lawrence H., P. O. Box 883, Stanford University, Cal.  
 Eiseman, B. J., Jr., 614 Ponce de Leon Ave., Atlanta, Ga.  
 Elsoffer, Harvey H., 321 S. Division St., Ann Arbor, Mich.  
 Finch, Geo., P. O. Box 134, Elkhart, Indiana.  
 Fleiss, Alois D., Ayacucho 1846, Buenos Aires, Argentina, S. Amer.  
 Flenner, Albert Lawrence, Chem. Dept., University of Maryland, College Park, Md.  
 Hall, J. H., James Island, near Victoria, B. C., Canada.  
 Henderson, William F., Mellon Institute, Pittsburgh, Pa.  
 Henley, Martin S., 316 W. Washington Ave., Jackson, Mich.  
 Hill, Mark, 1017 Speight Ave., Waco, Texas.  
 Hunter, H. Blound, 1506 Brown Ave., Norfolk, Va.  
 Keller, Harry H., 398 Plymouth Ave., Buffalo, N. Y.  
 Ladd, Culver S., Agricultural College, North Dakota.  
 Laselle, Percy, Box 72, Rickreall, Oregon.  
 Lichtenwalner, D. C., Box 258, Riverdale, Md.  
 Macfarlan, Edward J., 219 Law St., Darlington, S. C.  
 Martling, Francis H., 1053 Armstrong, Kansas City, Kans.  
 McCollum, Ella, Mansfield Depot, Conn.  
 McKinney, David S., 1019½ Hallam St., Pittsburgh, Pa.  
 Morine, L. G., Université de Montreal, 185 rue S. Denis, Montreal, Can.  
 Morse, Jared K., 5800 Blackstone Ave., Chicago, Ill.  
 Normand, Alexander Robert, Wilson College, Bombay, 7, India.  
 Otsubo, Takeo, 1010 Main St., Urbana, Ill.  
 Pedersen, Herman, P. O. Padang, Serai, South Kedah, Malay Peninsula.  
 Pietsch, Paul F., Department of Beverage Inspection, Jefferson City, Mo.  
 Plasencia, Leonel, Amargura 59, Havana, Cuba.  
 Quisumbing, Francisco A., College of Agriculture, University of the Philippines, Los Banos, P. I.  
 Rafferty, James A., 30 E. 42nd St., New York City.  
 Salisbury, Henry M., 85 9th Ave., New York City.  
 Schuh, Arthur, 3529 N. Hoyne Ave., Chicago, Ill.  
 Skinner, Eugene W., Doane College, Crete, Neb.  
 Starkey, E. B., University of Maryland, College Park, Md.  
 Suzuki, Rokuo, Aji-no-moto-kojo, Kawasaki-machi, Kanagawa-ken, Japan.  
 Tuttle, Donald E., 2369 Fairview Ave., Cincinnati, Ohio.  
 Watt, Howard R., 919 W. Main St., Norristown, Pa.  
 Watterson, Paul Eldred, Keeler, Cal.  
 Wickey, S. A., Box 164, Sugar City, Col.  
 Wiley, R. C., College Park, Md.  
 Williamson, Herbert P., 655 Yaddin St., Kingsport, Tenn.  
 Williamson, John F. G., 529 East State St., Trenton, N. J.

#### CORPORATION MEMBERS.

Ajax Rubber Company, Inc., Trenton, N. J.  
 Los Angeles Soap Co., 633 East First St., Los Angeles, Cal.

### MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.]

#### COLORADO SECTION.

The regular meeting of the Section occurred on September 26. John B. Ekeley, of the University of Colorado, spoke on "The Present Status of the American Dye Industry."

RUTH B. VERTREES, *Secretary*.

#### EASTERN NEW YORK SECTION.

At the meeting held on September 16, J. W. McBain, of Bristol University, England, gave a talk on "The Physical Chemistry of Soap." Following him, L. V. King, of McGill University, Canada, Ernst Cohen, of the University of Utrecht, Holland, and Paul Heyman, of the University of Ghent, Belgium, spoke briefly on educational methods in use in their particular institutions.

MARY R. ANDREWS, *Secretary*.

## INDIANA SECTION.

On September 27, Charles E. Ruby, associate professor of physical chemistry at the Massachusetts Institute of Technology, spoke before the members on "The Research at the Physical Chemistry Laboratory of the Massachusetts Institute of Technology."

GEORGE B. WALDEN, *Secretary*.

## LOUISVILLE SECTION.

The first fall meeting of the Section occurred on September 30, when C. E. Ruby, of the Massachusetts Institute of Technology, spoke on "The Work of a Pure Science Laboratory, and Its Relation and Importance to Industrial Research."

C. E. GEIGER, JR., *Secretary*.

## OMAHA SECTION.

The eighth meeting of the Section was held on April 10, when Arthur E. Hall of the American Smelting and Refining Company, spoke on "Bismuth and Its Recovery from Lead Ores."

On May 10, the ninth meeting was addressed by P. J. Deschavsky who discussed the Rochester Meeting. H. A. Senter performed experiments to illustrate the action of solid carbon dioxide.

E. M. PARTRIDGE, *Secretary*.

## American Field Service Fellowships for French Universities.

The Society for American Field Service Fellowships for French Universities will offer for open competition among graduates of American colleges and other suitably qualified candidates a number of fellowships, not to exceed twenty-five, for the purpose of encouraging advanced study and research in French Universities during 1922-23.

## THE FELLOWSHIPS.

The fellowships, of the annual value of \$200 and 10,000 francs, are granted for one year and are renewable for a second year. They may be awarded in the following fields of study:

Agriculture, Anthropology, Archaeology and History of Art, Architecture, Astronomy, Biology, Botany, Chemistry, Classical Languages and Literature, Criminology, Economics, Education, Engineering, English Language and Literature, Geography, Geology, History, Law, Mathematics, Medicine and Surgery, Oriental Languages and Literature, Philosophy, Physics, Political Science and International Law, Psychology, Religion, Romance Languages and Literature, Semitic Languages and Literature, Slavic Languages and Literature, Sociology, and Zoology.

Fellows will be required to sail to France not later than July 1st of the year in which the award is made, to matriculate in a French University for the following session, and to pursue studies in the field of science designated in their awards. They will be expected to send accounts of their studies together with reports of their progress from their instructors.

## DECEASED.

W. B. Cogswell, Solvay Process Co., Syracuse, N. Y. Died June 7, 1921.

Cyril S. Dawes, Colonial Ammunition Co., Ltd., Gordon St., Footscray, Victoria, Australia. Died March 5, 1921.

Frank N. Smalley, P. O. Box 832, Savannah, Ga. Died, 1921.

F. C. Weld, 263 Fairmount St., Lowell, Mass. Died, 1921.

# Proceedings.

## COUNCIL.

MEMBERS ELECTED BETWEEN SEPTEMBER 15 AND OCTOBER 15, 1921.

Blackburn, Paul V., 1565 Woodward Ave., Lakewood, Ohio.  
Carter, Albert S., Carnegie Institute of Tech., Pittsburgh, Pa.  
Ericksen, Andrew C., 34 Gillette Place, Newark, N. J.  
Fuss, Chester G., 609 South Limestone St., Lexington, Ky.  
Green, Frank W., P. O. Box 208, Little Falls, N. J.  
Hazard, C. H., 7 East 42nd St., New York City.  
Kirschberg, Bradley H., 317 Clinton St., Schenectady, N. Y.  
Lansingh, Van Rensselaer, 56 Pine St., New York City.  
Lavett, Chas. O., 831 Elmwood Ave., Buffalo, N. Y.  
Ledbetter, R. H., P. O. Box 297, Bessemer, Ala.  
McLain, Leigh J., Tecumseh, Michigan.  
Merritt, Matthew M., 76 Lafayette St., Salem, Mass.  
Riddle, Oscar, Carnegie Lab., Cold Spring Harbor, L. I., N. Y.  
Shank, John J., Waynesboro, Pa.  
Stallbaumer, Adrian L., St. Benedict's College, Atchison, Kans.  
Stones, Charles W., 36th Floor, 233 Broadway, New York City.  
Thorne, L. G., Alnarp, Akarp, Sweden.  
Von Hagen, Verda, 126 Husband St., Stillwater, Okla.  
Weber, Ione, 14 Morningside Ave., New York City.  
Widmer, J. Max, 1716 8th Ave., E., Cedar Rapids, Iowa.

### CORPORATION MEMBERS.

Metakloth Co., Inc., Lodi, N. J.  
Young Brothers Company, 6500 Mack Ave., Detroit, Mich.

## MEETINGS OF THE SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons,  
1709 G. St., N. W., Washington, D. C.)

### AMES SECTION.

The officers of the Ames Section for the ensuing year are as follows: F. E. Brown, chairman; E. I. Fulmer, vice-chairman; H. V. Wright, secretary-treasurer; and W. F. Coover, councilor.

H. V. WRIGHT, *Secretary.*

### ALABAMA SECTION.

The following officers for the Alabama Section have been elected: J. F. Carle, chairman; Theodore Ledbetter, vice-chairman; James T. MacKenzie, secretary-treasurer; B. B. Ross, councilor; and C. N. Wiley, J. J. Phillips, and A. G. Overton, executive committee.

JAMES T. MACKENZIE, *Secretary.*

### CALIFORNIA SECTION.

The 126th meeting of the Section occurred on October 7. The speakers were as follows: C. L. Alsberg, director, Carnegie Food Laboratory, Stanford University, on "Studies in Protein Chemistry;" and A. R. Olson, of the University of California, on "The Effect of X-Rays on Certain Chemical Reactions."

BRYANT S. DRAKE, *Secretary pro tem.*

## CINCINNATI SECTION.

The 244th meeting of the Section was held on October 5, when C. E. Ruby, of the Massachusetts Institute of Technology spoke on "The Work of a Pure Science Laboratory and Its Relation and Importance to Industrial Research."

C. H. LUND, *Secretary*.

## CLEVELAND SECTION.

The Section held its first meeting of the season on October 18 and had as its speaker, L. F. Vogt, of the Standard Chemical Company, who spoke on "Radium and its Production."

H. S. BOOTH, *Secretary*.

## CONNECTICUT VALLEY SECTION.

On October 15, Thomas B. Freas, of Columbia University, addressed the members of the Section on "Laboratory Apparatus and Appliances."

H. WESSELS, *Secretary*.

## DELAWARE SECTION.

A. H. Pfund, of the Johns Hopkins University, spoke before the Section, on October 19, taking as his subject the "Measurement of Color as Applied to Industrial Needs."

E. C. LATHROP, *Secretary*.

## DETROIT SECTION.

The 126th meeting of the Section was held on October 19, when the members were addressed by John A. Gann, of the Dow Chemical Company, his subject being "Dow Metal."

The following officers have been elected for 1921: J. C. Moore, chairman; F. O. Taylor, vice-chairman; William B. Templeton, Secretary; and W. G. Walker, treasurer.

WM. B. TEMPLETON, *Secretary*.

## EASTERN NEW YORK SECTION.

The 102nd meeting of the Section, held on October 14, had as its speaker, Lewis Knudson, of Cornell University, who spoke on "Some Investigations on the Organic Nutrition of Plants."

MARY R. ANDREWS, *Secretary*.

## INDIANA SECTION.

At the meeting of the Section, held on October 14, Gerald L. Wendt, of the University of Chicago, spoke on "New Chemistry for Old Chemists."

GEO. B. WALDEN, *Secretary*.

## LEHIGH VALLEY SECTION.

The Section held a meeting on September 28, devoted to a symposium on Engineering Education.

On October 21, H. W. Jordan, of Syracuse, N. Y., addressed the Section, his subject being "The Laws of Evolution that Control Chemistry and Engineering."

J. G. SMULL, *Secretary*.

## MILWAUKEE SECTION.

The regular meeting of the Section was held on October 7, when John A. Wilson, of Gallun & Sons Company, spoke on "The Histology of Skin and the Chemistry of Leather Manufacture."

O. A. CHERRY, *Secretary*.

## NEBRASKA SECTION.

The 99th meeting of the Section, held on September 28, had as its speaker, H. A. Spoehr, of the Carnegie Institution Laboratory, Carmel, Cal., his subject being "The Cosmical Function of Green Plants." On the following day, Doctor Spoehr spoke on "The Nature of the Photo Synthetic Process."

SAUL B. ARENSON, *Secretary*.

## NEW HAVEN SECTION.

The first fall meeting of the Section was held on October 11, at which time Guy C. Givens, director of the research laboratory of the Celluloid Zapon Company, spoke on "The Manufacture and Use of Lacquers."

BLAIR SAXTON, *Secretary*.

## NEW YORK SECTION.

The New York Section, which met on October 7, had as its speaker, E. M. Chamot of Cornell University, his subject being "The Microscope and How the Chemist can use it."

HERBERT G. SIDEBOTTOM, *Secretary*.

## NORTHEASTERN SECTION.

The regular meeting of the Section, held on October 14, was addressed by the following speakers: C. J. James, of New Hampshire College, "The Rare Earths;" and Grinnell Jones, of Harvard University, "The Pending Tariff Bill." Two reels of moving pictures on the subject of "The Making of Soap," were shown.

L. F. HAMILTON, *Secretary*.

## PHILADELPHIA SECTION.

On October 20, Hugh S. Taylor, of Princeton, spoke to the members of the Section, his subject being "The Absorption of Gases by Solids."

J. HOWARD GRAHAM, *Secretary*.

## PUGET SOUND SECTION.

The first fall meeting of the Section was held on September 29, and had as its speakers, Ray W. Clough and Carl R. Fellers, their subject being "Some Scientific Aspects of the Salmon Industry."

R. W. ELLISON, *Secretary*.

## RHODE ISLAND SECTION.

Charles Baskerville, head of the Department of Chemistry, College of the City of New York, addressed the members of the Section, October 18, on "Science and Civilization; The Role of Chemistry."

NELSON BARLOW, *Secretary*.

## ROCHESTER SECTION.

On October 13, Ellwood Hendrick spoke to the members of the section, his subject being "The Chemical Warfare of America."

ERLE M. BILLINGS, *Secretary*.

## SAINT LOUIS SECTION.

On October 3, R. S. Sherwin, of the Aluminum Ore Company, spoke to the members of the Section, his subject being "Metallurgy of Aluminum."

At a special meeting of the Section, held on October 15, H. M. Whelpley spoke on "The Mounds and Mound Builders."

H. A. CARLETON, *Secretary*.

## TOLEDO SECTION.

The regular monthly meeting of the Section, held on October 14, had as its speaker, James R. Withrow, of the Ohio State University, who spoke on "Modern Developments in Chemical Engineering Materials of Construction."

T. E. MOORE, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

H. H. Bartlett, at the regular meeting of the Section, on October 14, addressed the members on the subject of "Primitive Chemical Technology."

C. C. MELOCHE, *Secretary*.

## UNIVERSITY OF MISSOURI.

On September 16, J. E. Underwood, of Denver, Colo., spoke before the meeting of the Section, his subject being "A New Form of Apparatus for Separating and Purifying Radium Emanation from Radium Salts."

H. D. HOOKER, JR., *Secretary*.

## VIRGINIA SECTION.

The 44th meeting of the Section, was held on October 21. Eugene C. Bingham, of Lafayette College, addressed the Section on "Recent Work on Plasticity."

ROBERT F. McCracken, *Secretary*.

## WASHINGTON, D. C. SECTION.

The 321st meeting of the Section occurred on October 13, at which time Edwin E. Slosson, of the Science Service, addressed the members on "The Constructive Chemist."

J. B. REED, *Secretary*.

## WISCONSIN SECTION.

On October 19, the following speakers addressed the Section: J. E. Day, on "A Study of Some Manganese Compounds;" and C. S. Leonard, on "A Recent Visit to European Chemical Laboratories."

V. L. BOHNSON, *Secretary*.

## DECEASED.

S. C. Linbarger, Carborundum Co., Niagara Falls, N. Y., died September 10, 1921.

Joseph W. Richards, Lehigh University, South Bethlehem, Pa., died October, 1921.

Samuel S. Voorhees, Bureau of Standards, Washington, D. C., died September 23, 1921.

# Proceedings.

## DIRECTORS' MINUTES.

The Directors of the American Chemical Society met by call of President Smith at the Chemists' Club, at 3:30 P.M., on Saturday, November 5, with President Smith and Directors Rosengarten, Teeple, Talbot, and Parsons present.

The meeting was called especially to consider the resignation of Charles H. Herty as Editor of the *Journal of Industrial and Engineering Chemistry* and Director of the American Chemical Society News Service and to consider the election of his successor as immediate action was necessary. The following letter of resignation from Dr. Herty was received and ordered spread on the record:

New York,  
October 31, 1921.

Dr. EDGAR F. SMITH, President,  
American Chemical Society,  
Philadelphia, Pa.

*Dear Dr. Smith:*

It is with many feelings of poignant regret that I hereby tender my resignation of the office of Editor of the *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY*. It is my hope that the officers of the Society will accept the same and that my successor will be named just as promptly as possible.

I take this step for the reason that on last Friday evening at the meeting of the manufacturers of synthetic organic chemicals in Washington, D. C., I was unanimously elected President of a new organization there and then organized and named Synthetic Organic Chemical Manufacturers of the United States. When the information of the selection was first brought to me, I stated unequivocally that I could not accept it. Later in the evening I was called upon by a large delegation of manufacturers who urged my acceptance and I repeated my declination and the reasons therefor. However, after a three hours' conference they succeeded in putting the matter to me in such a way that I felt it my duty to accept, convinced that through this new channel I could perform a useful public service and perhaps be of even greater helpfulness to the chemists of the country than I could hope to be through continuation of the office of Editor. I therefore did accept.

I shall of course continue to look after the work of the *JOURNAL* until my successor takes office, though I shall be obliged to divide my time between the two organizations. However, I am convinced of the loyal coöperation of the members of our staff here and that there will be no diminution of the activities of the *JOURNAL*.

In conclusion, may I express to you and each officer and member of the American Chemical Society my heartfelt appreciation of that spirit of coöperation and support which has made my five years' incumbency of the office of Editor a continuous joy.

Sincerely yours,  
CHAS. H. HERTY,  
*Editor.*

The Directors voted to accept the resignation to take effect at the earliest possible moment, the exact date to be fixed by President Smith, and a letter of appreciation be sent Dr. Herty by President Smith for his services to the American Chemical Society. As Dr. Herty pressed for immediate release from his editorial duties in order that he might undertake the very important work of the Synthetic Organic Chemical Manufacturers of the United States and asked, if possible, that his successor should actively undertake the handling of the *Journal* by the first of December, the Directors decided that it was necessary to exercise the authority given them by the By-Laws and to act for the Council in the election of a successor to fill out the unexpired term of Dr. Herty, ending January 1, 1923. After careful consideration of some twenty suggestions, H. E. Howe was unanimously elected Editor of the *Journal of Industrial and Engineering Chemistry* and Director of the American Chemical Society News Service. It was voted that the salary of the new editor remain the same as at present and that, if found necessary, the editorial offices be removed to Washington.

It was voted that the Secretary should increase foreign postage on the Journal of Industrial and Engineering Chemistry and on the Journal of the American Chemical Society from seventy-five cents to \$1.00, the combined postage rate remaining, as at present, at \$2.50.

It was voted to call a meeting of the Directors to consider the annual budget on Saturday, December 10, at 3 p.m., at the Chemists' Club.

It was voted to authorize the Secretary, if found advisable, to arrange for a special train previous to the Birmingham Meeting to visit points of interest en route.

It was voted that, as President Smith has been appointed one of the technical members of the Disarmament Conference, the necessary funds to meet his expenses in Washington be appropriated.

It was voted that, in view of the changing nature of the American Chemical Society membership, it was inadvisable to issue an engraved certificate of membership for framing, as had been requested by a few members.

It was voted that in the opinion of the Directors it was unnecessary to register the title of Journal of Industrial and Engineering Chemistry as a trademark in the United States Patent Office, as suggested by one of our members, it being deemed that the copyright was sufficient.

The meeting then adjourned.

CHARLES L. PARSONS,  
*Secretary.*

## COUNCIL.

The following communication was sent to the Council on November 7th:

### COUNCIL OF THE AMERICAN CHEMICAL SOCIETY

Gentlemen:

November 7, 1921

It is with sincere regret that I have to announce to you the resignation of Chas. H. Herty, under date of October 31, 1921, as Editor of the Journal of Industrial and Engineering Chemistry and Director of the American Chemical Society News Service. As already announced in the public press, he has been elected President of the newly organized Association of Synthetic Organic Chemical Manufacturers. He has asked for immediate release, and his resignation has been accepted.

On account of the urgency and the fact that a letter ballot for nomination and election by the Council would require approximately two months, President Smith instructed me to call a meeting of the Directors to elect his successor, the Directors, under the Constitution, being the only body having the authority to act on all matters for the Council when the Council is not in session. The meeting was held Saturday afternoon, November 5th, at the Chemists' Club, New York City.

After careful consideration of the situation, the Directors unanimously elected H. E. Howe, Editor of the Journal of Industrial and Engineering Chemistry and Director of the American Chemical Society News Service, with the understanding that this election involved the removal of the offices to Washington, if accepted.

Mr. H. E. Howe has tentatively accepted the position, but states that he does not feel that he can permanently enter into the work and complete the unexpired term of Chas. H. Herty, ending December 31, 1922, without the assurance that the Council is in full accord with the Directors' action and that he will have their hearty support.

Will you, accordingly, mail to me at the earliest possible moment your opinion in the enclosed ballot envelope. No name should be attached thereto, as it is desired that every Councilor should feel entirely free to express his approval or disapproval of this action.

Yours very truly,

CHARLES L. PARSONS,  
*Secretary.*

The result of the vote was 152 approvals and 12 disapprovals.



## MEMBERS ELECTED BETWEEN OCTOBER 15 AND NOVEMBER 15, 1921.

Austin, Brother, C. S. C., 1324 N. Pennsylvania St., Indianapolis, Ind.  
 Ayer, Richard B., 49 Randolph Hall, Cambridge, 38, Mass.  
 Bartholomew, Tracy, Mellon Inst., University of Pittsburgh, Pittsburgh, Pa.  
 Biddle, Arthur, 428 Ardmore Ave., Trenton, N. J.  
 Boyden, E. Wynne, c/o A. I. Root Co., Medina, Ohio.  
 Burgess, Louis, 152 Avenue B., Bayonne, N. J.  
 Coyne, Bernard B., Morley Chem. Lab., Adelbert College, Cleveland, O.  
 Davis, Claude F., 219 West St., Stillwater, Okla.  
 Davis, Paul K., 446 Grand Ave., Brooklyn, N. Y.  
 Deller, A. William, R. F. D. No. 2, Allendale, N. J.  
 Dickinson, J. R., c/o Mrs. Saunders, University, Va.  
 Dillingham, Winthrop Bulkley, St. Anthony Hall, Williamstown, Mass.  
 Dodds, Herbert Henry, Box 191, La. State University, Baton Rouge, La.  
 Donald, Maxwell B., 12 Inman St., Cambridge, Mass.  
 Drobka, Frank J., 740 Langdon St., Madison, Wis.  
 Glass, Emanuel, Suffern, N. Y.  
 Gregory, Rev. P., Subiaco College, Subiaco, Ark.  
 Haines, Edward C., 1067 Beacon St., Brookline, Mass.  
 Hamilton, Russell, 343 Main St., Wareham, Mass.  
 Hara, Terutaro, Lab. of Applied Chemistry, Imperial University, Kyoto, Japan.  
 Henke, Clyde O., 430 E. Fourth St., Bloomington, Ind.  
 Jephcott, Harry, Glaxo Res. Lab., 56 Osnaburgh St., London, N. W. 1, Eng.  
 Jones, Chester A., 517 Iowa Ave., Iowa City, Iowa  
 Katz, Alexander, 2229 Creston Ave., New York City.  
 Kemmer, Raymond, 1439 W. Bancroft St., Toledo, Ohio.  
 Laub, Leon C., 124 Sussex Ave., Newark, N. J.  
 Leach, Winthrop W., Magnolia Petroleum Co., Beaumont, Texas.  
 Lum, Joe Woon, 155 Willoughby Ave., Brooklyn, N. Y.  
 Marks, B. R., Calydor, Gravenhurst, Ont., Canada.  
 Nesterowicz, J. J., 849 Fillmore Ave., Buffalo, N. Y.  
 Pierce, Dorothy Gordon, 50 Willard Court, Oberlin, Ohio.  
 Piron, Emil H., 43 Broad St., New York City.  
 Robertson, A. F., 373 Upham St., Melrose, Mass.  
 Rubin, Harold, 22 East 93rd St., New York City.  
 Schultz, Raymond, 660 61st Ave., Milwaukee, Wis.  
 Smith, Harrison P., 615 S. Virgil Ave., Los Angeles, Cal.  
 Smyth, Henry Field, School of Hygiene, University of Pa., Philadelphia, Pa.  
 Spicer, H. N., 101 Park Ave., New York City.  
 Taketa, Kichiro, Laboratory of Applied Chemistry, Kyoto, Japan.  
 Teberne, H. Olga, 2326 Camp St., New Orleans, La.  
 Tyndall, Arthur M., 9 Henleaze Gardens, Bristol, England.  
 Wedderburn, Augustus, 1454 Euclid St., N. W., Washington, D. C.  
 Worstell, Richard A., 353 College Ave., Valparaiso, Indiana.

## MEETINGS OF THE SECTIONS.

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

## AMES SECTION.

The 29th meeting of the Section, held on October 12, was addressed by W. K. Robbins, of Manchester, N. H., taking for his subject, "Science with Practice."

R. A. Gortner, head of the Agricultural Biochemical Department at the University of Minnesota, spoke before the members at the regular monthly meeting of the Section held on November 22, his subject being "Life Processes from the Colloidal Standpoint."

H. V. WRIGHT, *Secretary*.

## CALIFORNIA SECTION.

The 127th regular meeting of the Section was held on November 4, the following addresses having been made: "Science and Education," by Joel H. Hildebrand, of the University of California; "Felt Base Floor Covering," by W. H. Nutting, of the Paraffine Companies.

BRYANT S. DRAKE, *Secretary, pro tem.*

## CENTRAL TEXAS SECTION.

The following officers have been elected by the Section for 1922: C. C. Hedges, president; J. R. Bailey, vice-president; W. W. Battle, secretary-treasurer; and J. L. Brakefield, councilor.

W. W. BATTLE, *Secretary.*

## CHICAGO SECTION.

At the regular meeting of the Section, held on October 21, Paul E. Klopsteg, of the Leeds & Northrup Company, spoke on "Some Practical Aspects of Electrometric Analysis." Informal group meetings followed the address of the evening.

At the regular meeting of the Section, held on November 18, H. C. Parmelee, editor of Chemical and Metallurgical Engineering, addressed the members on "The Technical Magazine and Its Relation to Industry."

S. L. REDMAN, *Secretary.*

## CINCINNATI SECTION.

The 245th regular meeting of the Section, held on November 9, had as its speaker, R. S. Tour, of the University of Cincinnati, his subject being "Engineering Aspects of the Synthetic Ammonia Process."

C. H. LUND, *Secretary.*

## CLEVELAND SECTION.

"Some Technical and Scientific Applications of the Colloid Chemistry of Soaps and Proteins," was the subject of an address by Martin H. Fischer before the members of the Section on November 14.

H. S. BOOTH, *Secretary.*

## COLORADO SECTION.

At the regular meeting of the Section on November 28, Frank E. E. Germann, of the University of Colorado, spoke on "Thermal Analysis as a Method of Discovering New Compounds."

RUTH B. VERTRIES, *Secretary.*

## COLUMBUS SECTION.

On November 29, C. W. Foulk, of the Ohio State University, spoke to the members on the subject of "My Field of Research and What has been Accomplished in it."

EDWARD MACK, *Secretary.*

## CONNECTICUT VALLEY SECTION.

At the annual meeting of the Section, held on November 19, J. S. Chamberlain and L. B. Allyn addressed the members on "Vitamines." The following officers were elected for 1922: J. S. Chamberlain, chairman; G. Albert Hill, vice chairman; George B. Hogaboom, treasurer; Paul Serex, Jr., secretary; J. C. Andrews, Vernon K. Kriebble and W. H. Wooffindale, executive committee; C. A. Hoover and J. A. Newlands, councilors.

PAUL SEREX, JR., *Secretary.*

## DELAWARE SECTION.

The regular monthly meeting of the Section was held on November 30, when James Kendall, of Columbia University, spoke on "A Modified Ionization Theory."

E. C. LATHROP, *Secretary.*

## EASTERN NEW YORK SECTION.

On November 11; Dr. Edgar F. Smith, president of the American Chemical Society spoke before the members of the Section, taking as his subject "Early Organic Chemistry in America."

MARY R. ANDREWS, *Secretary*.

## GEORGIA SECTION.

The following program was given before the members of the Georgia Section, at the regular meeting held on November 5: "Architecture of the Atom," by J. S. Guy; "Chemical Industry in England," by T. C. Law; and a report on the New York meeting, by C. A. Butt.

J. S. BROGDON, *Secretary*.

## INDIANA SECTION.

Taking as his subject, "Life as a Chemical Profession," Benjamin Turner, of the Indiana Medical School, addressed the members of the local Section at the regular monthly meeting, held on November 11.

GEORGE B. WALDEN, *Secretary*.

## IOWA SECTION.

The first fall meeting of the Section was held on October 22. The principal address was given by Ernst Cohen, who discussed "The Diffusion Problem."

As a result of the recent election held by the Iowa Section, the officers to serve for 1922 are as follows: Edward Bartow, chairman; R. W. Getchell, vice chairman; L. Chas. Raiford, secretary-treasurer; J. N. Pearce, counselor.

L. CHARLES RAIFORD, *Secretary*.

## KANSAS CITY SECTION.

The 151st meeting of the Section was held on October 22, at which time J. E. Earnshaw, food and dairy commissioner of Kansas City, gave an address on "The Kansas City Milk Situation." F. B. Dains, of the University of Kansas, reported on the New York meeting.

The 152nd meeting of the Section, held on November 19 at the University of Kansas, Lawrence, Kansas, had as its speaker, E. C. Kinney, who spoke on "Copper Smelting." Attendance, 23%.

LEE E. CLARK, *Secretary*.

## LEXINGTON SECTION.

The 72nd meeting of the Section, which occurred on October 19, was a "get together" meeting. Several short addresses were made, followed by a round table discussion of subjects of interest to the Section. Attendance, 63%.

The following program was given at the 73rd regular meeting, held on November 9: "The Function of Grit in the Chicken Gizzard," by G. D. Buckner; and "No One Nose," by L. A. Brown and C. G. Fuss. Attendance, 44%.

S. D. AVERITT, *Secretary*.

## LOUISIANA SECTION.

At the first meeting of the season, held on October 21, the following program was rendered: "Conservation in Louisiana," by M. L. Alexander, Louisiana State Commissioner of Conservation; "Some Points in the Oil and Gas Situation," by C. S. Williamson, Jr.; and a brief report on the New York meeting, by C. E. Coates.

H. R. STEVENS, *Secretary*.

## MAINE SECTION.

At the meeting of the Section, held on November 9, M. R. Louria addressed the members, the subject of his paper being "Organic Electrochemistry."

J. N. CROMBIE, *Secretary pro tem*.

## MARYLAND SECTION.

On October 28, Charles L. Reese, of the du Pont Company, and Gen. Amos A. Fries, chief of the Chemical Warfare Service, addressed the members of the Maryland Section.

The following officers have been elected for 1922: F. M. Boyles, chairman; S. T. Powell, vice chairman; J. H. Wolfe, secretary-treasurer; Carl Haner, H. H. Lloyd, J. C. W. Frazer, Charles Neil, A. E. Marshall, and A. W. Warth, executive committee; E. E. Reid, J. H. Shrader, and W. B. D. Penniman, councilors.

J. H. WOLFE, *Secretary*.

## MICHIGAN AGRICULTURAL COLLEGE SECTION.

The first fall meeting of the Section was held on October 20, when J. G. Dean spoke on "The Recovery of Potash from Cement Kiln Gases." C. S. ROBINSON, *Secretary*.

At the regular meeting of the Section, held on November 22, D. L. Randall, of Albion College, spoke on "Chemistry in 1796." The following officers were elected for 1922: R. C. Huston, chairman; C. L. Bliss, vice chairman; Edward Eldridge, secretary; O. B. Winter, treasurer; and A. J. Patten, councilor. EDWARD ELDRIDGE, *Secretary*.

## MILWAUKEE SECTION.

At a special meeting of the Section, held on October 28, Frank C. Whitmore, of Northwestern University, addressed the members on "Organic Compounds of Mercury." The following officers were elected at this meeting to serve during 1922: Ralph M. Kibbe, chairman; Edwin J. Kern, vice chairman; O. A. Cherry, secretary; A. A. Chambers, treasurer; Henry C. Frey and C. A. Nash, councilors.

J. H. Walton, of the University of Wisconsin, addressed the meeting of the Section, held on November 18, his subject being "Some Factors Influencing the Rate of Crystal Growth." O. A. CHERRY, *Secretary*.

## MINNESOTA SECTION.

The following officers for the current year were elected at the meeting held on October 27: F. H. MacDougall, chairman; C. A. Mann, vice chairman; L. M. Henderson, Secretary; C. J. V. Pettibone, treasurer; R. A. Gortner and C. A. Mann, councilors.

At the regular monthly meeting, held on November 23, W. H. Hunter addressed the members on "Recent Researches in Organic Chemistry."

L. M. HENDERSON, *Secretary*.

## NASHVILLE SECTION.

The first meeting of the season, held on October 28, was given over to social features and to a discussion of plans for the year just beginning.

On November 18, two demonstration addresses, as follows, were delivered before the members of the Section: "Electrometric Titration with Use of Voltmeter as Indicator and the Measurement of  $p_H$  number," by L. J. Bircher, of the Vanderbilt University; and "The Arsenates of Sodium; the System  $As_2O_5-Na_2O-H_2O$ ; a Rapid Method of Determination of Total Arsenic in Insecticides," by W. A. Rudisill, of Vanderbilt University.

H. A. WEBB, *Secretary*.

## NEBRASKA SECTION.

The 100th regular meeting of the Section was held on October 27 at the University of Nebraska. J. M. Mayhew, of Lincoln, Nebraska, addressed the members on "Some Clinical Aspects of Blood Chemistry." Attendance, 40%.

The 101st regular meeting of the Section, held on November 28, had as its speaker, Roger Adams, of the University of Illinois, taking as his subject, "Researches on Synthetic Drugs in the United States." Attendance, 50%.

S. B. ARENSON, *Secretary*.

## NEW HAVEN SECTION.

James Kendall, of Columbia University, addressed the members of the Section on November 15, taking as his subject, "A Modified Ionization Theory."

BLAIR SAXTON, *Secretary*.

## NEW YORK SECTION.

Under the general heading of "Chemistry and Disarmament," the following program was given before the members of the Section, on November 18: "Chemical Research and Business," by Harrison E. Howe, of the National Research Council; "Recent Navy Tests," by Major H. S. Kimberly, and "Chemistry and Disarmament," by Francis P. Garvan, president of the Chemical Foundation.

HERBERT G. SIDEBOTTOM, *Secretary*.

## NORTHEASTERN SECTION.

The 170th regular meeting of the Section occurred on November 11, when the following program was presented to the members: "Chemical Clocks," by George Shannon Forbes, of Harvard College; "The Story of Rubber—What it is and What it Does," by Ralph E. Condor, of the Boston Woven Hose and Rubber Company; and "The Rubber Industry," moving pictures.

L. F. HAMILTON, *Secretary*.

## OKLAHOMA SECTION.

The Third Annual Meeting of the Oklahoma Section was held at Stillwater, Oklahoma, on October 28 and 29. The following program was carried out:

October 28—

Address—"Chemistry as an Experimental Science," by H. P. Cady.  
Announcements and Appointment of Committees, by Edwin DeBarr.  
Informal Reception to Dr. Cady.

October 29—

Presidential Address—by Edwin DeBarr.  
"Oil Field Practice in Handling Crude Oil Emulsions," by Sidney Born.  
"The Status of Chemistry in Oklahoma Teachers' Colleges," by Cliff R. Otto.  
"The Construction of Refinery Towers," by Julius Hansen.  
"Some Further Studies in Certain Organic Reactions in Which a Gas is Evolved," by Charles L. Nickolls.  
"The Petroleum Industry a Chemical Industry," by Charles K. Francis.  
"The Cost and Operation of a Shale Oil Still," by R. C. Beckstrom.  
"Some Further Uses for Aluminum Soap," by Hilton Ira Jones.  
"The Physiological Effect of Gossypol," by Paul Menaul.  
"The Nitrogen Distribution of the Two-Tenth Sodium Hydroxide Soluble Protein of Cottonseed Meal, Soy Beans, and Coconut," by W. G. Friedemann.  
"Some Quantitative Estimations by Means of the Spectroscope," by Edwin DeBarr.  
"The Effect of Starvation on the Composition of the Fats of Peanut-Fed Rabbits," by C. T. Dowell.  
"The Biologic Value of the Proteins of Peanuts, Soy Beans, and Coconuts," by C. T. Dowell.  
"A Talk on Helium," by H. P. Cady.  
Business Meeting and Annual Election.

At the above meeting, the following officers for 1922 were elected: Guy Y. Williams, president; Charles K. Francis, vice president; Hilton Ira Jones, secretary; J. B. Parks, treasurer; Edwin DeBarr, and C. T. Dowell, councilors.

HILTON IRA JONES, *Secretary*.

## OMAHA SECTION.

The 11th meeting of the Section occurred on October 11, when P. J. Deschavsky spoke on "Some Chemical and Industrial Aspects of Silk."

At the 12th meeting, held on November 8, R. N. Perkins discussed the "Sanitary Control of the Krug Park Swimming Pool at Omaha."

E. M. PARTRIDGE, *Secretary*.

## OREGON SECTION.

The first meeting of the season was held on October 29, at Reed College. Three addresses, as follows, were given: "Paint and Varnish Oils," by Paul Johnson; "Animal Fats and Oils," by Edward T. Luther; and "Soap Oils, Soap and Crude Glycerine," by H. Feldman.

PAGE R. BOYLES, *Secretary*.

## PHILADELPHIA SECTION.

On November 17, E. R. Weidlein, director of the Mellon Institute of Industrial Research, gave an illustrated lecture before the Section on the subject, "The Conservation of Heat in Power and Heating Systems by Means of 85% Magnesia, and the Applications of Magnesium Carbonate in the Chemical Industries."

J. HOWARD GRAHAM, *Secretary*.

## PITTSBURGH SECTION.

The 173rd meeting of the Section was held on October 20, when Alfred R. Powell, of the U. S. Bureau of Mines, spoke on "Sulfur in Coal and Coke."

The 174th meeting of the Section occurred on November 17. H. C. Bierman, of the Westinghouse Electric & Manufacturing Co., addressed the members on "Patents and the Chemist."

GEBHARD STREGMAN, *Secretary*.

## PUGET SOUND SECTION.

The October meeting of the Section was held under the auspices of the Olympian Chemical Club, at Tacoma, Wash., on October 22. The following program was carried out: Inspection of Tacoma Smelter, Informal Dinner and Meeting, and an address by Henry K. Benson, of the University of Washington, on "Chemical Industry in the State of Washington."

Wm. L. Haley, chief chemist of the Fisher Flouring Mills, spoke before the Section on November 19. His subject was "Chemical Control in the Milling Industry."

R. W. ELLISON, *Secretary*.

## RHODE ISLAND SECTION.

On November 25, Edgar F. Smith, president of the American Chemical Society, addressed the members of the Section, his subject being "Early Organic Chemistry in America."

SAMUEL T. ARNOLD, *Secretary*.

## ROCHESTER SECTION.

"What We Know About the Science of Nutrition," was the subject discussed by Elmer V. McCollom, of Johns Hopkins University, before the Section on October 17.

William H. Nichols, chairman of the Allied Chemical and Dye Corporation, spoke before the members of the Section on November 2, his subject being "America's Way Out of the Doldrums."

The 127th meeting of the Section, held on November 7, had as its speaker, Ralph Mellon, director of Clinical and Research Laboratories, Hahnemann Hospital, whose subject was "The Hydrogen Ion in Bacterial Environment and Bacterial Variability."

ERLE M. BILLINGS, *Secretary*.

## SAINT LOUIS SECTION.

On November 7, H. L. Ward, of Washington University, presented a paper before the members of the Section, his subject being "Physical Tests for the Purity of Organic Compounds."

H. A. CARLTON, *Secretary*.

## SAVANNAH SECTION.

The first fall meeting of the Section was held on October 13. Reports on the New York meeting were made by P. McG. Shuey and H. S. Bailey. This was followed by a symposium on "Nitrogen Determination," lead by R. F. Monsalvatge. Attendance, 43%.

F. I. Gibson, of the Southern Cotton Oil Co., spoke before the members of the Section, on November 10, his subject being "By-products of the Cotton Oil Industry." At this meeting the following officers for 1922 were elected: Eli H. Armstrong, chairman; P. McG. Shuey, vice chairman; Herbert P. Strack, secretary-treasurer; and Herbert S. Bailey, councilor.

HERBERT P. STRACK, *Secretary*.

## SOUTHEAST TEXAS SECTION.

The 18th meeting of the Section, held on November 4, had as its speaker, A. J. Hartsook, of the Rice Institute, taking as his subject, "Paper Making."

P. S. TILSON, *Secretary*.

## SOUTHERN CALIFORNIA SECTION.

The regular monthly meeting of the Section occurred on October 27, at the Radium Institute, Los Angeles, Calif., when an address was delivered by Rex Duncan on the subject, "The Chemistry and Physics of Radium," with special reference to its therapeutic action.

H. L. PAYNE, *Secretary*.

## SOUTH JERSEY SECTION.

On October 14, the members of the Section visited the plant of Joseph Bancroft and Sons Company, bleachers, dyers and finishers at Wilmington, Del.

The 11th regular meeting of the Section, held on November 22, had as its speaker, Edgar F. Smith, president of the American Chemical Society, who spoke on "Early Organic Chemistry in America." At this meeting the following officers for 1922 were elected: C. E. Burke, chairman; A. D. Holmes, vice chairman; M. H. Mahr, secretary-treasurer; and H. D. Gibbs, councilor.

H. W. MAHR, *Secretary*.

## SYRACUSE SECTION.

The 151st meeting of the Section was held on October 7. The first business to be transacted, after the dinner, was the election of the following officers for 1922: L. E. Wise, president; C. R. McCroskey, vice-president; W. B. Hicks, secretary; Louis Jordy, treasurer; A. C. Houghton and R. S. Fleming, councilors. Short speeches were made by several members of the section.

W. B. HICKS, *Secretary*.

## TOLEDO SECTION.

On November 11, the members of the Section heard an address by Frank G. Breyer, of the New Jersey Zinc Co., on the subject, "What Does my Program Mean to Me?"

T. E. MOORE, *Secretary*.

## UNIVERSITY OF ILLINOIS SECTION.

The 118th regular meeting of the Section was held on November 22. H. B. Lewis spoke on "The Importance of Sulfur in the Animal Organism." The following officers for 1922 were elected at this meeting: H. B. Lewis, chairman; J. H. Rudy, vice chairman; D. T. Englis, secretary; C. S. Marvel, treasurer; and Roger Adams and E. W. Washburn, councilors.

D. T. ENGLIS, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

Ernst Cohen, director of the Van't Hoff Laboratory, University of Utrecht, Holland, delivered lectures on November 1 and 2 before the Section, taking as his subject, "The Metastability of Matter and Its Bearings on Chemistry and Physics."

C. C. MELLORE, *Secretary*.

## VERMONT SECTION

On November 4, George Shannon Forbes, of Harvard University, spoke before the members of the Section, his subject being, "Modern Theories of Photochemical Reactions."

E. C. JACOBS, *Secretary*.

## VIRGINIA SECTION.

The 45th meeting of the Section was held on November 18. The address of the evening was by Graham Edgar on "Radiation as a Factor in Chemical Reactions."

ROBERT F. McCRACKAN, *Secretary*.

## WASHINGTON, D. C. SECTION.

The 322nd meeting of the Section occurred on October 25 at the Cosmos Club, when the following program was presented:

Presentation of the American Chemical Society's Portrait of Joseph Priestley, Discoverer of Oxygen, to the National Museum.

Acceptance of the Portrait by Charles D. Walcott, Secretary of The Smithsonian Institution.

"Development of Chemistry in the United States," by Edgar F. Smith, President of the American Chemical Society.

"Organization of the American Chemical Society at the Home of Priestley," by F. W. Clarke.

The 323rd meeting of the Section was held on November 10. Brief talks were made by Charles E. Munroe, W. D. Bigelow, R. B. Sosman, and other past presidents of the Section.

J. B. REED, *Secretary*.

## WISCONSIN SECTION.

The following program was presented before the members of the Section at the regular monthly meeting held on November 16: "The Decomposition of Nitrogen Pentoxide in Solution," by Roger H. Lueck; and "Hydrogen Persulfide," by J. H. Walton.

V. L. BOHNSON, *Secretary*.

## DECEASED.

George H. Ellis, 1818 Wesley Ave., Evanston, Ill. Died July 12, 1921.

Murray J. Etkin, 1352-46th St., Brooklyn. Died, 1921.

H. M. Gray, Como Chemical Co., Kokomo, Ind. Died July 3, 1921.

Lyman G. Jordan, Bates College, Lewiston, Maine. Died Feb. 27, 1921.

E. K. Kanet, 1503 Preston Ave., Akron, Ohio. Died, 1921.

Kate MacDermid, 2703 Bloomington Ave., Minneapolis, Minn. Died June 1921.

H. B. Schmidt, 3223 Spring Grove Ave., Cincinnati, Ohio. Died April 29, 1921.

Alexander Reid Whitehall, P. O. Box 394, Morgantown, Va. Died October 25, 1921.

Arthur G. Williams, 83rd St. and Ditmas Ave., Brooklyn, N. Y. Died, 1921.





**I. A. R. I. 75.**

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